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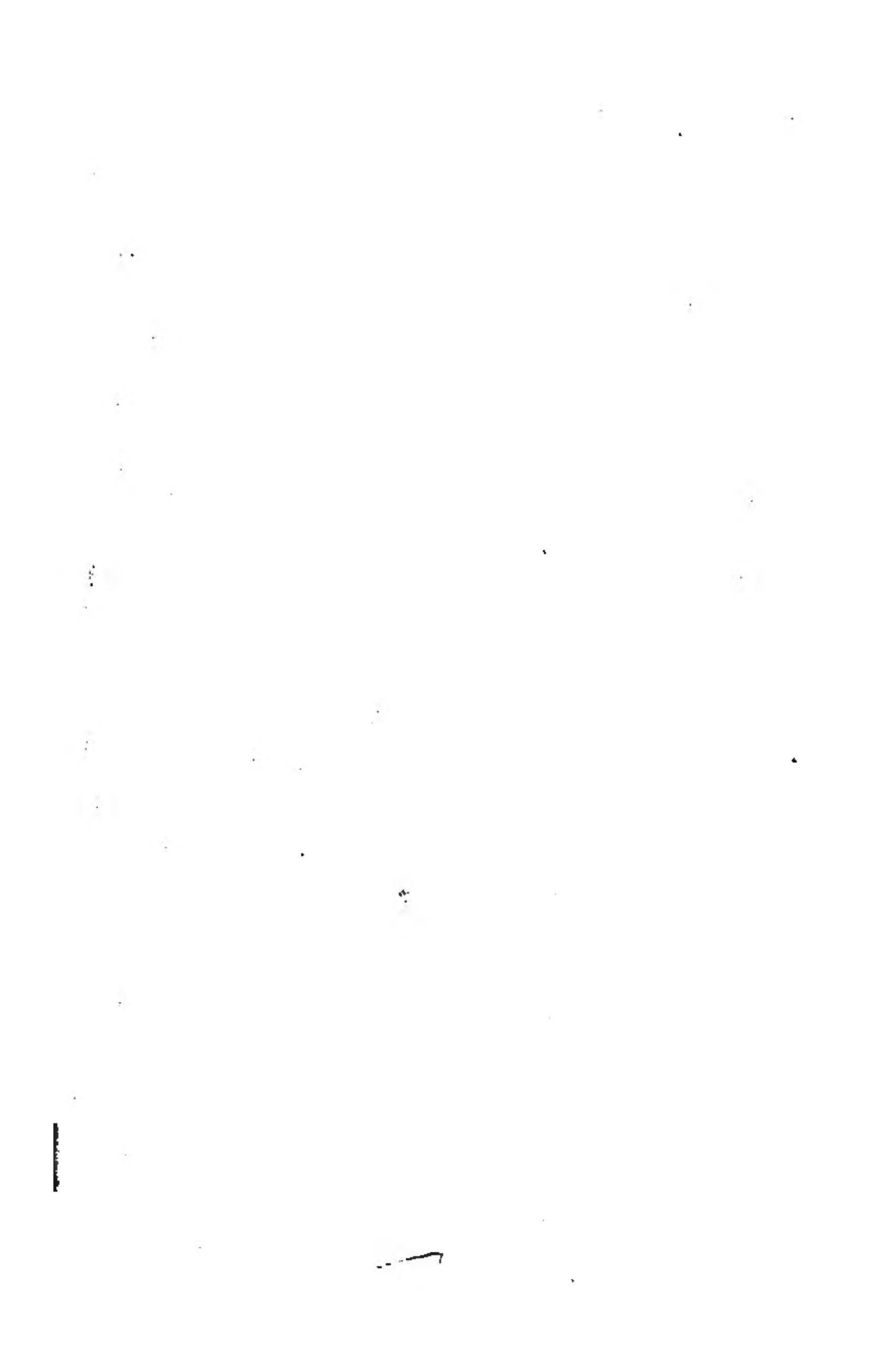
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# STANDARD METHODS OF CHEMICAL ANALYSIS

A MANUAL OF ANALYTICAL METHODS AND GENERAL  
REFERENCE FOR THE ANALYTICAL CHEMIST  
AND FOR THE ADVANCED STUDENT

EDITED BY

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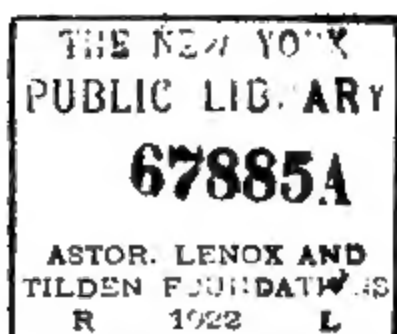
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VOLUME II



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TO MY FATHER,

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WILFRED W. SCOTT

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**DETERMINATION OF BITUMINOUS SUBSTANCES. INCLUDING  
ASPHALTS, TARS AND PITCHES**

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## RUBBER

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## EXPLOSIVES

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**VOLUME II**



# ACIDIMETRY AND ALKALIMETRY

WILFRED W. SCOTT

The volumetric determination of a free acid or a free base may be accomplished with rapidity and accuracy by neutralization with a known quantity of standard base or alkali as the case may require. The point of neutralization or "end point" is ascertained by means of certain compounds called indicators, which have a different color in acid solutions than in alkaline solutions, the point of transition from one color to the other occurs at the point of neutralization. This end point may also be recognized by the electrometric method by measuring the change of potential that occurs with the change of concentration of the hydrogen ions in the solution. This potential change is usually large and abrupt at the end point.<sup>1</sup>

**Indicators.** The change of color of indicators is attributed to a rearrangement of atoms in the molecule or to the fact that in certain cases the ions have a different color than the undissociated molecule.<sup>2</sup> In making acidimetric or alkalimetric titrations it must be remembered that the choice of indicators is important. In titrating phosphoric acid, for example, methyl orange and phenolphthalein indicate decidedly different end points. This difference in indicators is shown in the following table by Thompson.<sup>3</sup> The numerals refer to the number of atoms of hydrogen displaced by monatomic metals, such as sodium or potassium, when the indicator shows the neutral point.

Acids		Methyl Orange Cold	Phenolphthalein		Litmus	
Name	Formula		Cold	Hot	Cold	Hot
Sulphuric.....	H <sub>2</sub> SO <sub>4</sub>	2	2	2	2	2
Hydrochloric.....	HCl	1	1	1	1	1
Nitric.....	HNO <sub>3</sub>	1	1	1	1	1
Thiosulphuric.....		2	1	2	2	2
Carbonic.....	H <sub>2</sub> CO <sub>3</sub>	0	1 dil.	0		0
Sulphurous.....	H <sub>2</sub> SO <sub>3</sub>	1	1			
Hydrosulphuric.....		0	1 dil.	0		0
Phosphoric.....	H <sub>3</sub> PO <sub>4</sub>	1	2			
Arsenic.....	H <sub>3</sub> AsO <sub>4</sub>	1	2			
Arsenious.....	H <sub>3</sub> AsO <sub>3</sub>	0			0	0
Nitrous.....	HNO <sub>2</sub>	indicator destroyed	1		1	
Silicic.....	H <sub>2</sub> SiO <sub>4</sub>	0			0	0
Boric.....	H <sub>3</sub> BO <sub>3</sub>	0				
Chromic.....	H <sub>2</sub> CrO <sub>4</sub>	1	2	2		
Oxalic.....	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>		2	2	2	2
Acetic.....	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>		1		1 nearly	
Butyric.....	HC <sub>4</sub> H <sub>7</sub> O <sub>2</sub>		1		1 nearly	
Succinic.....	H <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>		2		2	
Lactic.....	HC <sub>3</sub> H <sub>5</sub> O <sub>3</sub>		1		1	
Tartaric.....	H <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>		2		2	
Citric.....	H <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>		3			

<sup>1</sup> J. C. Hostetter and H. S. Roberts, J. Am. Chem. Soc., 41, 1337 (1919).

<sup>2</sup> Theory of indicators—Scientific Foundations of Analytical Chemistry by McGowan Waddell, J. Phys. Chem., 2, 171, 1898. Stieglitz, J. Am. Chem. Soc., 25, 1112, 1903; Am. Chem. J., 42, 115, 1909. Hewitt, Analyst, 33, 85, 1908. Noyes, J. Am. Chem. Soc., 32, 815, 1910. Thorpe Dictionary of Applied Chemistry, Vol. 1, 34-37.

<sup>3</sup> Volumetric Analysis, Sutton, Tenth Edition, page 44. R. T. Thomson, J.S.C., 1. 12. 432.



There are two general classes of indicators; (a) Those highly sensitive to weak acids. In this class we have phenolphthalein, turmeric, rosolic acid. (b) Those insensitive to very weak acids, such as carbonic, hydrosulphuric, boric acids. Among this list are methyl orange, methyl red, lacmoid, cochineal, iodeosin. These indicators are specially sensitive to bases.

Methyl orange, methyl red, phenolphthalein, lacmoid and litmus are the most commonly used indicators for acidimetry and alkalimetry. The following table shows the best conditions for the use of each:

INDICATOR	CONDITION OF SOLUTION	GENERAL USE IN TITRATION
<b>Methyl orange.</b> acids = red alkalies = yellow.	Cold solution only.	Hydrates, carbonates, bicarbonates, sulphides, arsenites, silicates, borates of sodium potassium, ammonium, calcium, magnesium, barium, etc.
<b>Methyl red.</b> As above.	Cold solution only.	Especially adapted for titration of weak bases such as $\text{NH}_4\text{OH}$ .
<b>Phenolphthalein.</b> acids = colorless alkalies = red.	Cold solutions.	Alkaline hydrates, the mineral acids, organic acids, e.g., oxalic, citric, tartaric, acetic. The indicator very sensitive to acids and adapted to titration of weak acids—carbonic acid, etc.
	Hot solutions.	The indicator is sensitive in hot solutions to the above. It is generally used in hot solutions for titration of acids combined with comparatively weak bases.
<b>Litmus.</b> acids = red alkalies = blue.	Cold solutions.	Hydrates of Na, K, $\text{NH}_3$ , Ca, Ba, etc. Silicates and arsenates of Na and K, $\text{HNO}_3$ , $\text{H}_2\text{SO}_4$ , $\text{HCl}$ and $\text{H}_2\text{C}_2\text{O}_4$ .
	Hot solutions.	In addition to above neutral and acid carbonates of K, Na, Mg; the sulphides and silicates of Na, K.
<b>Lacmoid.</b> In alcohol acids = red alkalies = blue.	Cold solutions.	The alkaline and alkaline earth hydrates, the arsenates, borates, mineral acids, many salts of metals which are acid to litmus and neutral to lacmoid, e.g., sulphates and chlorides of iron, copper and zinc, hence of value in determining free acids in their presence.
	Hot solutions.	In addition to the above, carbonates and bicarbonates of K, Na, Ca, Sr, Ba, etc.

In general, methyl orange, methyl red and lacmoid are especially sensitive to bases, but not so sensitive to acids and are not used for weak acids. Phenolphthalein is especially sensitive to acids and is of value in titrating weak acids. Litmus is commonly used as a test indicator (litmus paper) though with careful preparation, it is valuable for general acid and alkali titration.

The acid in the indicator must be weaker than the acid which it is required to determine by its means. Methyl-orange, for example, is a fairly strong acid, and is not sensitive to carbonic, hydrocyanic, boric, oleic acids; on the other hand, phenolphthalein, being an extremely weak acid, is decomposed by organic acids,  $\text{H}_2\text{CO}_3$ , etc., hence is of value in determination of these acids.

## ULTIMATE STANDARDS

Sulphuric and hydrochloric acids are generally used as the ultimate standard acids. Benzoic acid and other acids are also used.

Sodium carbonate is the best of the alkali standards. This salt may be prepared in exceedingly pure form. It is generally used as the basic material for the volumetric standardization of the standard acid.

## Preparation of Pure Sodium Carbonate

**Bicarbonate of Soda** made by the Ammonia-Soda process may be obtained in exceedingly pure form. The impurities that may be present are silica, ammonia, lime, arsenic, sodium chloride and sodium sulphate. With the exception of silica and lime the impurities may be readily removed by washing the bicarbonate of soda several times with cold water and decanting off the supernatant solution of each washing from the difficultly soluble bicarbonate. The washing is continued until the material is free from chlorine, as sodium chloride is the principal impurity, and its removal leaves an exceedingly pure product. The bicarbonate is dried between large filter papers in the hot air oven ( $100^{\circ}\text{C}.$ ).

**Standard Sodium Carbonate** is made from this pure sodium bicarbonate by heating at  $290^{\circ}\text{C}.$  to  $300^{\circ}\text{C}.$  in an electric oven. If a constant-temperature oven is not available a simple oven may be improvised by use of a sand bath and a large beaker or a sheet-iron cylinder covered at the upper end as shown in Fig. 75. A thermometer passing through this shield registers the temperature of the material, within a large platinum crucible. This crucible rests upon a triangle, so that the bicarbonate is entirely surrounded by an atmosphere of comparatively even temperature.

The sodium bicarbonate is converted to the carbonate. Constant weight will be obtained in about five or six hours. When the material no longer loses weight it is cooled in a desiccator and bottled for use, preferably in several small, glass-stoppered bottles. For exceedingly accurate work the material is analyzed and allowance made for the impurities that may still remain. The error caused by any such impurities is so small that for all practical purposes it may be neglected.

This purified sodium carbonate is the ultimate standard for acidimetric and alkalimetric volumetric analysis.

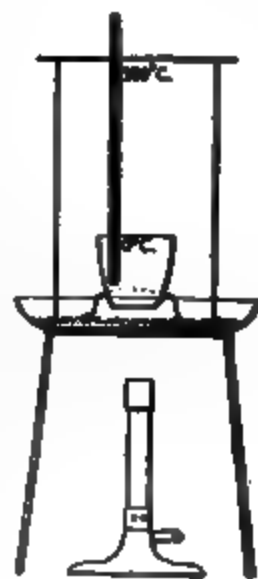


FIG 75.

## PREPARATION OF STANDARD ACID

## Standard Sulphuric Acid

Fifty-two per cent sulphuric acid is in equilibrium with the average moisture present in the air of the laboratory; acid of this concentration is recommended for the standard stock solution.<sup>1</sup>

Pure 94 to 97%  $\text{H}_2\text{SO}_4$  is diluted with sufficient water so that its gravity is about 1.4200 (42.7° Bé.). The acid is well mixed and poured into small clean and dry glass-stoppered sample bottles of about 200-cc. capacity. The bottles are carefully sealed and placed aside for use as desired. To determine the exact strength of this standard acid a portion is standardized against the sodium carbonate, prepared according to directions given.

**Method of Standardization. Procedure.** A catch weight of about 10 grams of the acid is weighed out in a weighing bottle or 100-cc. beaker (10 cc. = approximately 13 grams) and placed aside for titration. The amount of sulphuric acid in the sample (weight of sample multiplied by per cent divided by 100) is neutralized by 1.0808 times its weight of sodium carbonate. As an excess of acid is necessary to drive out all the carbonic acid the following formula is used—(grams  $\text{H}_2\text{SO}_4$   $\div$  0.05)  $\times$  1.0808 = weight of  $\text{Na}_2\text{CO}_3$  required.

The required amount of sodium carbonate is weighed and transferred to a 600-cc. Erlenmeyer flask and 100 cc. of water added. The acid is carefully poured into the flask and the rinsings of the weighing bottle or beaker added. The solution is boiled for 15 minutes to expel  $\text{CO}_2$ . A small filtering funnel inserted in the neck of the flask prevents loss during the boiling of the acid and carbonate mixture. The excess of acid is titrated with N/5  $\text{NaOH}$ , using phenolphthalein indicator, the caustic being added drop by drop until a faint permanent pink color is obtained.

(The sulphuric equivalent to the  $\text{NaOH}$  added) + (weight of  $\text{Na}_2\text{CO}_3 \times 0.9252$ ) = weight of pure  $\text{H}_2\text{SO}_4$  present in the sample.

**Notes.**  $\text{CO}_2$ -free water should be taken in all titrations with phenolphthalein. The indicator contains 1 gram of the compound per liter of 95% alcohol. One cc. of indicator of this strength is required for each titration.

Results should agree to within 0.05%.

The temperature of the acid should be observed at the time of standardisation and this noted with results on the bottles containing the standard samples. The coefficient of expansion is .00016 + per degree F. risen in temperature or .000293 per degree C. per cc. of solution.

<sup>1</sup> Ninety-three thousand pounds of sulphuric acid, with an exposed surface of 1200 sq. ft. and depth of 10 in., had decreased in strength from 86 per cent to 52.12 per cent  $\text{H}_2\text{SO}_4$ , after standing in a lead pan, protected from the rain, for 42 days (Sept. 9th to Oct. 21st, 1916). Air was bubbled through a two-liter sample of this acid for seven consecutive days, when the solution was tested and found to contain 52.18 per cent  $\text{H}_2\text{SO}_4$ . The average temperature of the laboratory was 74° F., the average vapor of the air (7 tests) was 0.2223 gram  $\text{H}_2\text{O}$  per standard cubic foot. The average humidity for September and October was 68 per cent; the average temperature 62° F. The average humidity for the past 33 years was 72 per cent; average temperature 57° F.

**Normal Sulphuric acid**<sup>1</sup> contains 49.043 grams of  $\text{H}_2\text{SO}_4$  per liter of solution. To make a liter of the normal acid the amount of the standard acid required is

calculated by the formula  $\frac{100 \times 49.043}{\text{per cent } \text{H}_2\text{SO}_4 \text{ in standard}} = \text{grams standard acid}$

necessary. The acid is weighed out in a small beaker, a slight excess being taken (0.1 gram). The acid is washed into a liter flask and made to volume. An aliquot portion is standardized against the standard sodium carbonate. The solution may now be adjusted to the exact strength required.

**Example.**<sup>1</sup> If 25 cc. of the acid is found to contain 1.25 grams  $\text{H}_2\text{SO}_4$ , we find the amount of dilution required as follows: 25 cc. of N/1  $\text{H}_2\text{SO}_4$  should contain 1.226075

grams, therefore  $1.226075 : 25 :: 1.25 : x$ , and  $x = \frac{25 \times 1.25}{1.226075}$ . Then  $x$  minus 25 = the amount of water required for 25 cc. Total dilution = dilution for 25 multiplied by the volume of acid remaining in the flask divided by 25 = cc. water required to make a normal acid solution.

**Fifth normal and tenth normal acids**<sup>1</sup> may be prepared by diluting the normal acid to five or ten volumes as the case requires.

**Gravimetric Methods. Precipitation as  $\text{BaSO}_4$ .** Sulphuric acid may be standardized by precipitating as  $\text{BaSO}_4$  according to the procedure given for sulphur.  $\text{BaSO}_4 \times 0.4202 = \text{H}_2\text{SO}_4$ .

**Determination as  $(\text{NH}_4)_2\text{SO}_4$ .** To 10 cc. of the acid diluted to 50 cc. in a large platinum dish is added  $\text{NH}_4\text{OH}$  until the acid is neutralized and a faint odor of ammonia is perceptible. The solution is evaporated to dryness on the water bath and dried at  $100^\circ \text{C}$ . for half an hour. The residue is weighed as  $(\text{NH}_4)_2\text{SO}_4$ .  $(\text{NH}_4)_2\text{SO}_4 \times 0.7422 = \text{gram } \text{H}_2\text{SO}_4$ .

### Standard Hydrochloric Acid

This acid is occasionally preferred by chemists to sulphuric acid as a standard. At the constant boiling-point, with pressure of 760 mm., hydrochloric acid has a definite composition of 20.242%  $\text{HCl}$ . For every 10 mm. increase in pressure the percentage drops .024 and for every 10 mm. decrease in pressure the percentage rises .024%  $\text{HCl}$ . Advantage is taken of this fact in the preparation of standard hydrochloric acid. Strong, pure  $\text{HCl}$  is distilled, the first 25 or 30 cc. being rejected. The distillate is bottled in 200-cc. glass-stoppered bottles and sealed, a portion being reserved for standardization. The acid is best standardized against sodium carbonate, using the formula, Weight of  $\text{HCl}$  weighed for analysis minus  $0.05 \times 1.4533 = \text{Na}_2\text{CO}_3$  required. As in case of  $\text{H}_2\text{SO}_4$  the  $\text{Na}_2\text{CO}_3$  is weighed out, placed in an Erlenmeyer flask with the acid and boiled to expel  $\text{CO}_2$ . The excess of  $\text{HCl}$  is titrated with standard caustic.  $\text{N}/5 \text{ NaOH} = 0.0072836 \text{ gram } \text{HCl} \text{ per cc.}$

The exact weight of  $\text{Na}_2\text{CO}_3 \times 0.6881 = \text{HCl}$ . To this add  $\text{HCl}$  obtained by  $\text{NaOH}$  titration = total  $\text{HCl}$  in the sample taken.

The exact amount of  $\text{HCl}$  being known, normal acid containing 36.468 grams  $\text{HCl}$  per liter may be made, and by diluting further, fifth normal and tenth normal acids obtained.

**Gravimetric Determination of Hydrochloric Acid by Precipitation as AgCl.** Hydrochloric acid may be standardized by precipitation with silver nitrate solution by the procedure for determination of chlorine.  $\text{AgCl} \times 0.2544 = \text{HCl}$ . It is advisable to heat the sample, diluted to a convenient volume, and add the hot silver nitrate in slight excess of that required by HCl, the amount of the reagent being calculated, e.g., mol. wt. HCl : mol. wt.  $\text{AgNO}_3 :: \text{Wt. HCl in sample} : x$ .

---

### Benzoic Acid Standard

Benzoic acid may be obtained in exceedingly pure form by melting the resublimed acid in a covered platinum dish in a constant-temperature oven, at a temperature of  $140^\circ \text{C}$ . The acid is poured into test-tubes, cooled, and the sticks bottled for use. The acid does not take up moisture to any appreciable extent, even when exposed to the air for some time, so that it may be weighed without danger of absorption of moisture.

### Standard Caustic Solution

Standard normal sodium hydroxide is made by dissolving approximately 50 grams of NaOH sticks with 1 to 2 grams of  $\text{Ba(OH)}_2$  in 200 to 300 cc. of water and diluting to 1000 cc. The caustic is standardized against normal  $\text{H}_2\text{SO}_4$ , using phenolphthalein indicator. The solution is adjusted to the exact strength desired by addition of distilled water.

NOTE.—The addition of  $\text{Ba(OH)}_2$  is made to precipitate the carbonate in the caustic, as this would interfere with titrations in presence of phenolphthalein. As the presence of barium would produce a cloudiness with  $\text{H}_2\text{SO}_4$ , it is advisable to add only an amount sufficient to precipitate the carbonate.

## STANDARD BURETTES

Burettes used for this work should be carefully checked for accuracy of delivery.

For accurate titration of acids or alkalis it is advisable to have a titration of 75 to 100 cc. Since the straight 100-cc. burette if graduated to twentieths of a cc. would be too long for convenient handling, the chamber burette is used. The chamber located in the upper portion of the apparatus holds 75 cc., the lower portion drawn out into a uniform-bore tube is graduated in twentieths of a cc. Each tenth of a cc. has a mark passing entirely around the tube so that there will be no error in reading, the eye being held so that the mark appears to be a straight line drawn across the tube. The burette is enclosed in a large tube filled with distilled water and carrying a thermometer. The burette is connected, by means of an arm at the base, with a reservoir of standard acid. The cut, Fig. 76, shows the apparatus connected ready for use.

If vapor is lost from the standard reagents and this replaced by dry air, as in the common practice, the solution gradually changes in strength. A simple and ingenious device, designed by H. W. Herig (Gen. Chem. Co.), is shown at the top of Fig. 76, which overcomes this difficulty. The air drawn into the reagent bottle is purified and saturated with moisture by passing it through sodium hydroxide. A mercury valve relieves the pressure if expansion of air in the reagent bottle occurs due to rise of temperature.

*Note.* The chamber burette shown in Fig. 76 was designed at the Laurel Hill Laboratory, General Chemical Company.

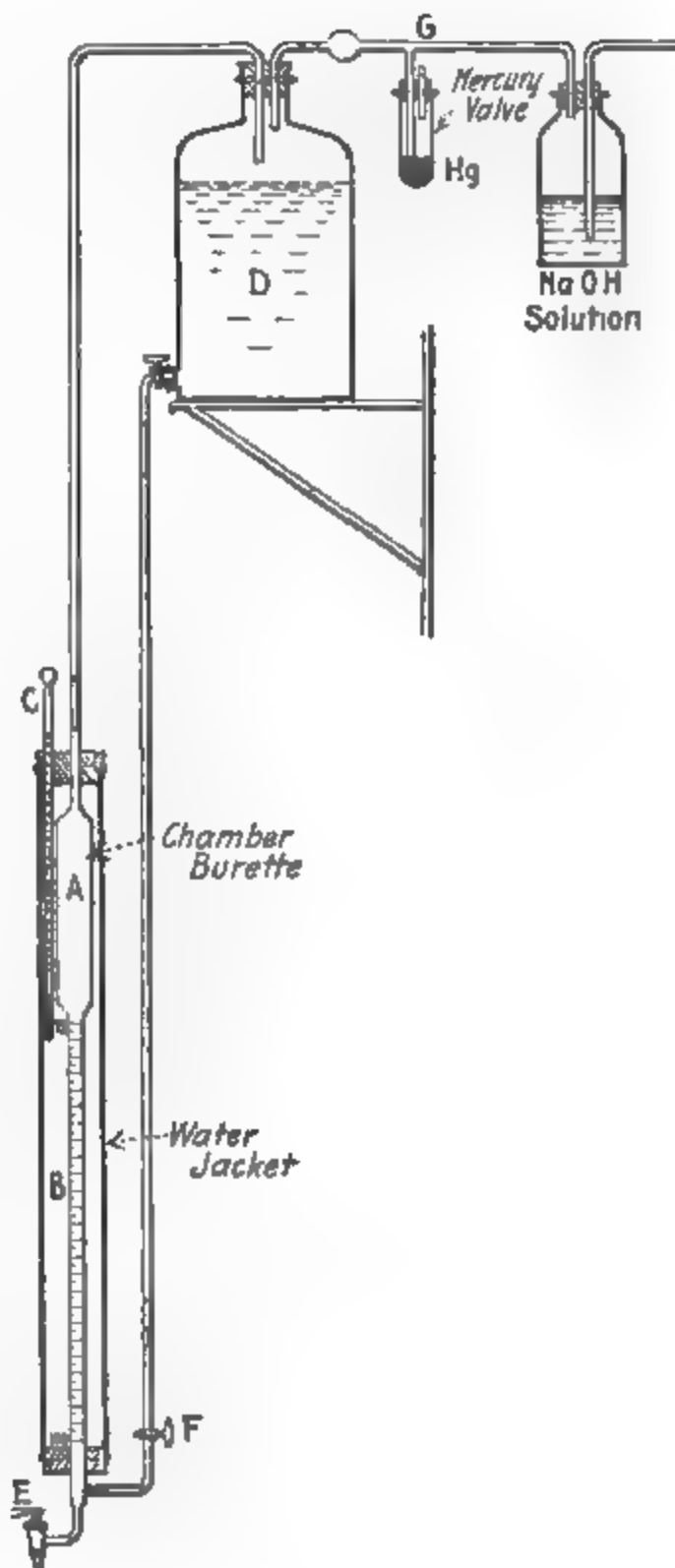


FIG. 76.

## Titration of Acids and Alkalies

In the acid titration the sample is conveniently titrated in a white porcelain casserole. This gives a white background that enables the analyst to see the end-point. The caustic is run into the acid, to within a few cc. of the end-point, rapidly and then cautiously to a faint change of color—faint pink with phenolphthalein or an orange-yellow with methyl-orange. Phenolphthalein is generally preferred to acid titrations.  $\text{CO}_2$ -free caustic and water should always be used.

## METHODS OF WEIGHING ACIDS

## Dilute Acids Non-Volatile under Ordinary Conditions

Dilute acids may be weighed directly in a beaker, weighing bottle or ordinary pipette (see directions given later) by measuring out the approximate amount desired. Since a burette reading from 75-cc. to 100-cc. should be used for this work it will be necessary to take such an amount of the acid as will require a titration between these extremes. This may be accomplished by taking the specific gravity of the acid and referring to the table for the approximate strength. From this the volume necessary may readily be calculated.

**Example.** The case will be taken where a 75-cc. to 100-cc. burette is being used and the titration is to be made with normal caustic solution, the acid titrated is sulphuric acid. The capacity of the burette is  $75 \times 0.049 = 3.675$  grams  $\text{H}_2\text{SO}_4$  to  $100 \times 0.049 = 4.9$  grams  $\text{H}_2\text{SO}_4$ . (For  $\text{HCl}$  the capacity would be 2.74 to 3.65 grams  $\text{HCl}$  and for  $\text{HNO}_3$  it would be 4.73 to 6.3 grams  $\text{HNO}_3$ ).

Suppose the sulphuric acid has a sp.gr. of 1.1600. From the table for  $\text{H}_2\text{SO}_4$  we find that this acid is 22.25%  $\text{H}_2\text{SO}_4$ , then 1 cc. contains  $1.16 \times 22.25$  divided by 100 = 0.2581 gram  $\text{H}_2\text{SO}_4$ . Since the capacity of the burette is 3.675 to 4.9 grams  $\text{H}_2\text{SO}_4$ , we must weigh between  $\frac{3.675}{.2225}$  to  $\frac{4.9}{.2225}$  grams of the acid; to get this we should take  $\frac{3.675}{.2581}$  to  $\frac{4.9}{.2581}$  cc., that is to say, 14.5 to 18.5 cc. of the acid, which will weigh 16.8 grams to 21.5 grams.

## Weighing Strong Acids, Fuming or Volatile under Ordinary Conditions

The acid must be confined during weighing and until it is mixed with water or standard caustic. The best forms of apparatus include the following:

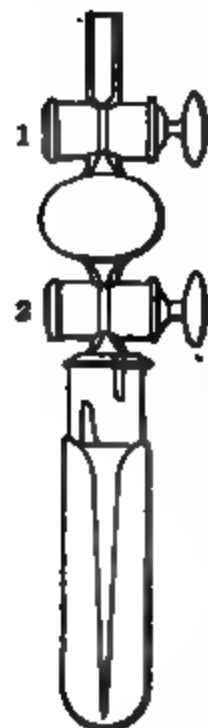


FIG. 77.  
Lunge-Ray  
Pipette.

**Lunge-Ray Pipette.** The pipette is shown in Fig. 77. Two glass stop-cocks confine the acid in a bulb. The lower part of the pipette is protected by a ground-on test-tube. The dry pipette is weighed. Cock 2 is closed and 1 opened and a vacuum produced in the bulb by applying suction at the upper end of pipette and closing stop-cock 1 with suction still on. The sample may now be drawn into the pipette by immersing the lower end in the sample and opening the stop-cock 2, the vacuum producing the suction. The increased weight = acid drawn in. The pipette is emptied by running the acid under water.

**Dely Weighing Tube.**<sup>1</sup> This form of weighing tube has proven to be of exceptional value, to the busy works-chemist, in the analysis of oleum and mixed acids. Both speed and accuracy are gained by its use. The apparatus, shown in the cut on page 1011, consists of a long glass tube of small bore, wound in a spiral coil. Fig. 78.

The sample of acid is drawn into the weighed coil by applying suction through a rubber tube attached to A and drawing in the required amount of acid, a mark, ascertained by a previous run being made, to indicate the point to which the acid is drawn. The

<sup>1</sup> J. G. Dely, Chemist, Gen. Chem. Co.

tip *B* is carefully wiped off with tissue paper and the tube and sample weighed. The weight of the tube deducted gives the weight of the sample.

The apparatus is now inclined so that the acid runs back into the crook at *C* to a point marked on the wall of the tube, in order to expel as much air as possible from this end. A rubber tube filled with water is attached to *A*, the other end of the rubber tube being connected to a bottle containing distilled water. A glass bead, such as is used in rubber-tipped burettes, fitting snugly in this tube, regulates the flow of water. The Dely tube is now inverted, the tip being immersed in 150 cc. to 200 cc. of distilled water in a 4-in. casserole—Fig. 78. By pressing gently on the bead, water is slowly admitted in the tube, forcing the acid before it. The acid and water are separated by a bubble of air. Before forcing out the last half-inch of acid, the tube connected to the water supply is disconnected and the weak acid from the casserole drawn back into the Dely tube for two or three inches, then again the acid is almost entirely expelled by water from the reservoir and the procedure repeated. This is to absorb the  $\text{SO}_2$  gas that invariably is present in the bubble of air above mentioned, which would be lost if forced out directly by the water column. In order to facilitate this last step it is well to have a short rubber tube attached to the Dely tube, and a glass tip in the tube connected with the reservoir of water. The acid in the casserole, upon washing out the Dely tube, is titrated with standard caustic according to the procedure for titration of acids.

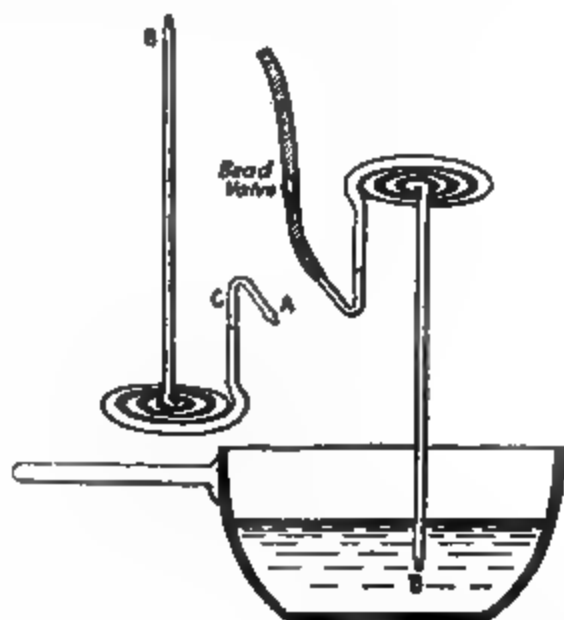


FIG. 78.

Dely Weighing Tube in Operation.

The tube is dried after washing with alcohol, followed by ether, by heating on an asbestos mat on a hot plate, dry air being aspirated through.

**Snake Weighing Tube.** The snake tube is a simple device that may be easily made by an amateur glass-blower. It is made out of a glass tube 8–10 ins. long, slightly thinner than a lead pencil. One end of the tube is drawn out to capillarity. The tube has a double bend, as shown in the illustration. It is so made that it rests on the double bend with the ends inclined upward to prevent the outflow of the acid. Fig. 79.

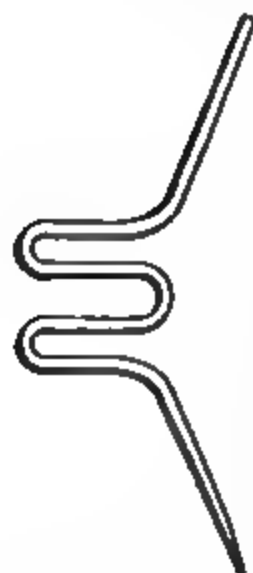


FIG. 79.

Snake Tube.

The tube is dried with alcohol, ether and air treatment, as in case of the Dely tube. After weighing the empty tube, acid is drawn into it by suction through an attached rubber tube. The capillary end that has dipped into the sample is wiped dry with tissue paper. The acid and tube are weighed and the acid estimated by difference.

The acid is run into 150 cc. of water in a casserole, the flow being regulated by the index finger pressed against the larger end of the tube. With careful regulation of the flow, practically no bumping occurs. With a small capillary opening it is not necessary to place the finger over the larger end of the tube as the acid flow will be slow. The tube should be kept in motion to prevent bumping from



overheating any one portion. Kicking back of the acid indicates that the capillary end of the tube is too large. When the contents of the tube have run out, the tube is rinsed by sucking up some acid from the casserole and allowing it to run out, repeating several times. Suction may be applied by means of a rubber bulb attached to the tube. The acid is now titrated with standard caustic, using phenolphthalein indicator.

**Blay-Burkhard Graduated Weighing Burette.** This apparatus, designed by V.

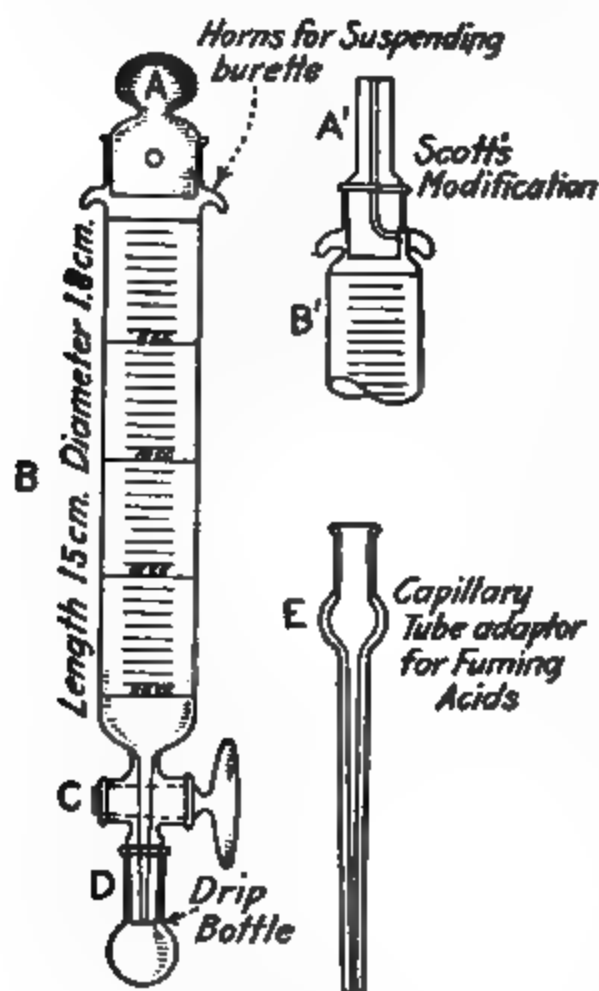


FIG. 80.—Blay-Burkhard Graduated Weighing Burette.

L. Blay and W. E. Burkhard, General Chemical Company, is used for weighing acids or other liquids. The form for general use is shown in Fig. 80. The burette is graduated in half cc. divisions, from 0 to 20 cc. An apparatus half this size is used for oleum, where a 2-cc. sample is sufficient for a determination. For the purpose of running the sample under water a capillary tube (E, Fig. 80) with ground joint, is attached to the burette. This tube is placed in the solution during titration. The burette is provided with a glass vented stopper (A) on the top, and a glass cap for the tip, both having ground joints, to prevent escape of fumes from the sample.

The Editor has modified the apparatus by replacing the fragile cap (A) by a tube stopper with capillary vent (see A', Fig. 80). The vent to the air is opened or closed by a slight turn of this stopper. By means of this tube acid may be drawn into the burette according to the Lunge-Ray pipette procedure. With these burettes a man can control his work very accurately and save a great amount of time, both in weighing and manipulation.

In the analysis of strong oleum, about 50 grams of neutral Glauber salt are placed in a casserole containing water, and the fuming acid allowed to flow under the undissolved salt. The violent reaction of the acid with water is thus avoided. The tube E, Fig. 80, should be made of fused silica.

The glass-bulb method is still used for analysis of strong oleum. The acid weighed in a sealed tube of known weight is mixed with water by breaking the bulb in a stoppered bottle containing water, the acid is cooled and titrated as usual.

## ANALYSIS OF MURIATIC ACID

(Commercial Hydrochloric Acid)

### Total Acidity and Hydrochloric Acid

The usual titration with standard caustic gives the total acidity, including, in addition to hydrochloric acid, nitric and sulphuric acids which may occur in the commercial product. The acidity due to these acids is deducted from the total acidity to find the actual HCl in the muriatic acid.

A catch weight, 10 to 15 grams of the acid, is weighed in a weighing bottle, or a large snake tube, or the Dely tube, as in case of oleum analysis, and the acid allowed to mix with water in a casserole; methyl-orange indicator is added and the acid titrated with standard normal caustic solution, the red color fading to a lemon-yellow. A fraction of a drop of the alkali will cause the change when the end-point has been reached.

One cc. N/1 NaOH = 0.03647 g. HCl.

**NOTE.** Hydrochloric acid may be determined gravimetrically by precipitating the chloride with silver nitrate— $\text{HCl} + \text{AgNO}_3 = \text{AgCl} + \text{HNO}_3$ , or by the volumetric methods for the determination of chlorine. See Chlorine.

### Determination of Impurities in Commercial Hydrochloric Acid. Free Chlorine

Five cc. of the acid are diluted to 10 cc., about 5 cc. of fresh starch solution added and a few drops of 5% KI solution together with about 1 cc. of dilute  $\text{H}_2\text{SO}_4$ . A blue color indicates free chlorine. This color may be matched in a Nessler tube with a standard. It is possible to determine .0001% chlorine on a 5-cc. sample.

### Nitric Acid or Nitrates in Hydrochloric Acid

About 5 cc. of the hydrochloric acid is cautiously added to 75 cc. of 95%  $\text{H}_2\text{SO}_4$ , the HCl being introduced under the surface of the sulphuric acid. The nitric acid may now be titrated with standard ferrous sulphate by the procedure for the direct determination of nitric acid and nitrates. (Method of Scott and Bowman.) The ferrous sulphate test for nitric is delicate. Traces of nitric acid produce a pink coloration; larger amounts a reddish brown to dark brown. The color is permanent when an excess of ferrous sulphate has been added. See page 1024.

### Sulphuric Acid and Sulphates in Hydrochloric Acid

**Free  $\text{H}_2\text{SO}_4$ .** Fifty cc. of the sample is evaporated in a platinum dish (steam bath) to dryness or until the HCl has been expelled. A few drops of water are added and the material again taken to dryness (steam bath). The residue is taken up with water and titrated with N/10 NaOH, using methyl-orange indicator. One cc. = 0.0049043 gram  $\text{H}_2\text{SO}_4$ .

**Total Sulphates.** Fifty cc. of the muriatic acid is evaporated to about 5 to 10 cc. and then diluted to about 200 cc. and heated to boiling. Total  $\text{SO}_4$  is now precipitated by adding  $\text{BaCl}_2$  solution as in case of determination of total sulphur. The precipitated  $\text{BaSO}_4$  includes the free  $\text{H}_2\text{SO}_4$  and the combined  $\text{SO}_4$ .  $\text{BaSO}_4 \times 0.4202 = \text{H}_2\text{SO}_4$ .

### Arsenic in Hydrochloric Acid

Commercial muriatic acid may contain arsenic. This is best determined by the Gutzeit Method given in detail under Arsenic. 10 cc. of sample is usually sufficient for this determination. If much arsenic is present the distillation method may be followed, using a 25 to 50-cc. sample. The distillate is titrated with standard iodine according to procedure given for arsenic by the iodine titration, page 43.

### Barium Chloride in Hydrochloric Acid

Fifty cc. is evaporated to dryness and then over a low flame to expel  $\text{SO}_2$ . The residue is taken up with 1 cc. of 1 : 1  $\text{HCl}$  and 50 cc. of water. 1 cc.  $\text{H}_2\text{SO}_4$  is added and the precipitated  $\text{BaSO}_4$  filtered off and weighed. If silica is present in the sample its weight should be deducted.  $\text{BaSO}_4 \times 0.8923 = \text{BaCl}_2$ .

### Total Solids and Silica

One hundred cc. of the  $\text{HCl}$  in a platinum dish is evaporated to dryness and the residue ignited and weighed. 5 cc. of  $\text{HF}$  is added with a few drops of  $\text{H}_2\text{SO}_4$  and the solution again evaporated and ignited. *The first weight = total solids. The loss of weight in the second ignition =  $\text{SiO}_2$ .*



The Gravity tables given in the following pages have been developed with considerable care. By means of these one is able to obtain quickly and with fair degree of accuracy the strength of the acid or alkali of which the gravity is ascertained.

The following precautions should be observed in making hydrometer tests:

1. The hydrometer should be clean and dry, and at the temperature of the liquid, before immersing to make a reading.

2. The vessel in which the observation is made should be of clear glass of suitable size and shape, to allow the hydrometer to float freely (about  $\frac{2}{3}$  inch greater in diameter than the hydrometer bulb) and of sufficient height to enable full reading of the hydrometer (i.e., height greater than the length of the hydrometer).

3. The liquid should be thoroughly mixed by means of a stirrer reaching to the bottom of the vessel. There should be no air bubbles in the liquid or clinging to the sides of the vessel or the hydrometer.

4. The hydrometer is slowly immersed in the liquid, slightly beyond the point where it floats and is then allowed to float freely.

5. The reading is made with the line of vision horizontal to the plane and as near as possible to this. The point is taken where this surface line cuts the hydrometer scale.

7. The temperature of the liquid is taken before and after the reading and allowance made for variation of the temperature from standard conditions as indicated in the tables.

**References.** Cir. 16, 4th edition, Feb. 23, 1916, U. S. Bureau of Standards.

Sulphuric Acid Handbook by Thos. J. Sullivan, McGraw-Hill Book Co.

Thorpe Dictionary of Applied Chemistry, pp. 103-114. Longmans, Green and Co.

## HYDROCHLORIC ACID

BY W. C. FERGUSON

Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.	Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.
1.00	1.0069	1.38	1.40	14.25	1.1090	21.80	21.68
2.00	1.0140	2.80	2.82	14.50	1.1111	22.22	22.09
3.00	1.0211	4.22	4.25	14.75	1.1132	22.64	22.50
4.00	1.0284	5.68	5.69	15.00	1.1154	23.08	22.92
5.00	1.0357	7.14	7.15	15.25	1.1176	23.52	23.33
5.25	1.0375	7.50	7.52	15.50	1.1197	23.94	23.75
5.50	1.0394	7.88	7.89	15.75	1.1219	24.38	24.16
5.75	1.0413	8.26	8.26	16.0	1.1240	24.80	24.57
6.00	1.0432	8.64	8.64	16.1	1.1248	24.96	24.73
6.25	1.0450	9.00	9.02	16.2	1.1256	25.12	24.90
6.50	1.0469	9.38	9.40	16.3	1.1265	25.30	25.06
6.75	1.0488	9.76	9.78	16.4	1.1274	25.48	25.23
7.00	1.0507	10.14	10.17	16.5	1.1283	25.66	25.39
7.25	1.0526	10.52	10.55	16.6	1.1292	25.84	25.56
7.50	1.0545	10.90	10.94	16.7	1.1301	26.02	25.72
7.75	1.0564	11.28	11.32	16.8	1.1310	26.20	25.89
8.00	1.0584	11.68	11.71	16.9	1.1319	26.38	26.05
8.25	1.0603	12.06	12.09	17.0	1.1328	26.56	26.22
8.50	1.0623	12.46	12.48	17.1	1.1336	26.72	26.39
8.75	1.0642	12.84	12.87	17.2	1.1345	26.90	26.56
9.00	1.0662	13.24	13.26	17.3	1.1354	27.08	26.73
9.25	1.0681	13.62	13.65	17.4	1.1363	27.26	26.90
9.50	1.0701	14.02	14.04	17.5	1.1372	27.44	27.07
9.75	1.0721	14.42	14.43	17.6	1.1381	27.62	27.24
10.00	1.0741	14.82	14.83	17.7	1.1390	27.80	27.41
10.25	1.0761	15.22	15.22	17.8	1.1399	27.98	27.58
10.50	1.0781	15.62	15.62	17.9	1.1408	28.16	27.75
10.75	1.0801	16.02	16.01	18.0	1.1417	28.34	27.92
11.00	1.0821	16.42	16.41	18.1	1.1426	28.52	28.09
11.25	1.0841	16.82	16.81	18.2	1.1435	28.70	28.26
11.50	1.0861	17.22	17.21	18.3	1.1444	28.88	28.44
11.75	1.0881	17.62	17.61	18.4	1.1453	29.06	28.61
12.00	1.0902	18.04	18.01	18.5	1.1462	29.24	28.78
12.25	1.0922	18.44	18.41	18.6	1.1471	29.42	28.95
12.50	1.0943	18.86	18.82	18.7	1.1480	29.60	29.13
12.75	1.0964	19.28	19.22	18.8	1.1489	29.78	29.30
13.00	1.0985	19.70	19.63	18.9	1.1498	29.96	29.48
13.25	1.1006	20.12	20.04	19.0	1.1508	30.16	29.65
13.50	1.1027	20.54	20.45	19.1	1.1517	30.34	29.83
13.75	1.1048	20.96	20.86	19.2	1.1526	30.52	30.00
14.00	1.1069	21.38	21.27	19.3	1.1535	30.70	30.18

## HYDROCHLORIC ACID (Continued)

Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.	Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.
19.4	1.1544	30.88	30.35	22.5	1.1836	36.72	36.16
19.5	1.1554	31.08	30.53	22.6	1.1846	36.92	36.35
19.6	1.1563	31.26	30.71	22.7	1.1856	37.12	36.54
19.7	1.1572	31.44	30.90	22.8	1.1866	37.32	36.73
19.8	1.1581	31.62	31.08	22.9	1.1875	37.50	36.93
19.9	1.1590	31.80	31.27	23.0	1.1885	37.70	37.14
20.0	1.1600	32.00	31.45	23.1	1.1895	37.90	37.36
20.1	1.1609	32.18	31.64	23.2	1.1904	38.08	37.58
20.2	1.1619	32.38	31.82	23.3	1.1914	38.28	37.80
20.3	1.1628	32.56	32.01	23.4	1.1924	38.48	38.03
20.4	1.1637	32.74	32.19	23.5	1.1934	38.68	38.26
20.5	1.1647	32.94	32.38	23.6	1.1944	38.88	38.49
20.6	1.1656	33.12	32.56	23.7	1.1953	39.06	38.72
20.7	1.1666	33.32	32.75	23.8	1.1963	39.26	38.95
20.8	1.1675	33.50	32.93	23.9	1.1973	39.46	39.18
20.9	1.1684	33.68	33.12	24.0	1.1983	39.66	39.41
21.0	1.1694	33.88	33.31	24.1	1.1993	39.86	39.64
21.1	1.1703	34.06	33.50	24.2	1.2003	40.06	39.87
21.2	1.1713	34.26	33.69	24.3	1.2013	40.26	40.09
21.3	1.1722	34.44	33.88	24.4	1.2023	40.46	40.32
21.4	1.1732	34.64	34.07	24.5	1.2033	40.66	40.55
21.5	1.1741	34.82	34.26	24.6	1.2043	40.86	40.78
21.6	1.1751	35.02	34.45	24.7	1.2053	41.06	41.01
21.7	1.1760	35.20	34.64	24.8	1.2063	41.26	41.24
21.8	1.1770	35.40	34.83	24.9	1.2073	41.46	41.48
21.9	1.1779	35.58	35.02	25.0	1.2083	41.66	41.72
22.0	1.1789	35.78	35.21	25.1	1.2093	41.86	41.99
22.1	1.1798	35.96	35.40	25.2	1.2103	42.06	42.30
22.2	1.1808	36.16	35.59	25.3	1.2114	42.28	42.64
22.3	1.1817	36.34	35.78	25.4	1.2124	42.48	43.01
22.4	1.1827	36.54	35.97	25.5	1.2134	42.68	43.40

Sp. Gr. determinations were made at 60° F., compared with water at 60° F.  
 From the Specific Gravities, the corresponding degrees Baumé were calculated by the following formula: Baumé = 145 - 145/Sp. Gr.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

## ALLOWANCE FOR TEMPERATURE:

10-15° Bé. - 1/40° Bé. or .0002 Sp. Gr. for 1° F.

15-22° Bé. - 1/30° Bé. or .0003 " " " 1° F.

22-25° Bé. - 1/28° Bé. or .00035 " " " 1° F.

AUTHORITY - W. C. FERGUSON.

This table has been approved and adopted as a Standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER, JAS. L. MORGAN,  
 HENRY HOWARD, ARTHUR WYMAN,  
 A. G. ROSENGARTEN,

New York, May 14, 1903.

Executive Committee.

## HYDROCHLORIC ACID

Specific Gravity. 15° In Vacuo.	Per Cent HCl by Weight.	1 Liter con- tains Grams HCl.	Specific Gravity 15° In Vacuo.	Per Cent HCl by Weight.	1 Liter con- tains Grams HCl.	Specific Gravity 15° In Vacuo.	Per Cent HCl by Weight.	1 Liter con- tains Grams HCl.
1.000	0.16	1.6	1.075	15.16	173	1.145	28.61	328
1.005	1.15	12	1.080	16.15	174	1.150	29.57	340
1.010	2.14	22	1.085	17.13	180	1.152	29.95	345
1.015	3.12	32	1.090	18.11	197	1.155	30.33	353
1.020	4.13	42	1.095	19.06	209	1.160	31.52	366
1.025	5.15	53	1.100	20.01	220	1.163	32.10	373
1.030	6.15	64	1.105	20.97	232	1.165	32.49	379
1.035	7.15	74	1.110	21.92	243	1.170	33.46	392
1.040	8.16	85	1.115	22.86	255	1.171	33.65	394
1.045	9.16	96	1.120	23.82	267	1.175	34.42	404
1.050	10.17	107	1.125	24.78	279	1.180	35.39	418
1.055	11.18	118	1.130	25.75	291	1.185	36.31	430
1.060	12.19	129	1.135	26.70	303	1.190	37.23	443
1.065	13.19	141	1.140	27.66	315	1.195	38.16	456
1.070	14.17	152	1.1425	28.14	322	1.200	39.11	469

COMPOSITION OF CONSTANT BOILING  
HYDROCHLORIC ACID\*

Pressure mm. of Mercury.	Per Cent of HCl.	Grams constant boiling distillate for 1 mol. HCl.
770	20.218	180.390
760	20.242	180.170
750	20.266	179.960
740	20.290	179.745
730	20.314	179.530

Temperature of constant boiling hydrochloric acid is 108.54° at 763 mm.  
Specific gravity 1.09620<sup>1</sup>.

\* Hulett and Bonner, Jour. Am. Chem. Soc. xxxi, 396.

## ANALYSIS OF HYDROFLUORIC ACID

The following constituents—hydrofluosilicic sulphuric and sulphurous acids—commonly occurring with hydrofluoric acid, are determined in the analysis, along with the hydrofluoric acid, by titration. Generally the acid contains a slight residue upon ignition. The titrations are made in presence of  $\text{KNO}_3$ , first ice cold, and then completed at  $80^\circ \text{C}$ . or more. The cold titration gives the hydrofluoric, sulphuric and sulphurous acids and one-third of the hydrofluosilicic acid and upon heating the titration gives the remaining two-thirds of the  $\text{H}_2\text{SiF}_6$ , the following reactions taking place. Titration cold,  $\text{H}_2\text{SiF}_6 + 2\text{KNO}_3 = \text{K}_2\text{SiF}_6 + 2\text{HNO}_3 (= \frac{1}{3} \text{H}_2\text{SiF}_6)$ . The liberated  $2\text{HNO}_3$  requires  $2\text{NaOH}$ . Titration hot,  $\text{K}_2\text{SiF}_6 + 4\text{NaOH} = 4\text{NaF} + 2\text{KF} + \text{SiO}_2 + 2\text{H}_2\text{O} (\frac{2}{3} \text{H}_2\text{SiF}_6)$ .

The sulphuric acid is determined by titration with  $\text{NaOH}$ , upon expulsion of the accompanying more volatile acids. Sulphurous acid is determined by titration with standard iodine.

**Special Apparatus.** Chamber burette graduated from 75 to 100 cc. in  $\frac{1}{10}$  cc. as described under the determination of sulphuric acid, oleum, mixed acids, etc.

**Platinum weighing tube.** Length about 5 cm., diameter 1.4 cm. The tube fitted with a platinum cap with a loop top to facilitate removal by means of a platinum wire.

**Lead thief for sampling.**

**Special Reagents.**

**Normal solution of  $\text{NaOH}$ .** 1 cc. = .04903 gram  $\text{H}_2\text{SO}_4$ .

**N/10 Iodine solution.** 1 cc. = .0041 gram  $\text{H}_2\text{SO}_4$ .

**Phenolphthalein indicator, and Starch solution.**

## Details of Procedure. Total Acidity and Hydrofluosilicic Acid

A catch weight of the acid is taken by pouring the acid by means of the thief or directly from the paraffine bottle into the platinum weighing bottle, such a weight being taken as will require a titration of from 75 to 100 cc. of the normal caustic solution. (This may be judged by a preliminary run if the approximate value is not known.)

About 10 cc. of a saturated solution of  $\text{KNO}_3$  is poured into a large platinum dish (capacity about 125 cc.), and chipped ice added. About 50 cc. of N/1  $\text{NaOH}$  solution is run in from a burette and three drops of the strong phenolphthalein added. The platinum weighing bottle containing the sample is inverted beneath the surface of the caustic, the cover cautiously removed from the bottle by means of a heavy platinum wire, so as to allow the acid to mix very gradually with the standard  $\text{NaOH}$  (rapid addition is apt to cause loss of acid by fumes). Standard N/1  $\text{NaOH}$  is added from the burette until the first permanent pink color is obtained. (The end-point will be uncertain and fading unless the solution is kept

cold— $0^\circ \text{C}$ .) The reading of the burette is noted—total  $\frac{\text{N/1 NaOH}}{\text{Wt. of sample}} = \text{A}$ .

The dish is now placed on a hot plate and the solution warmed to about  $80^\circ \text{C}$ . and the titration completed with the N/1  $\text{NaOH}$  solution to a permanent pink. Additional cc. required divided by weight of sample = B. (See calculation at close of procedure.)



### Sulphuric Acid in Hydrofluoric Acid

About 5 grams of the sample are weighed in the platinum capsule and transferred to a large platinum dish, the capsule being rinsed out into the dish with water. The solution is evaporated on the steam bath to small volume (the evaporation is assisted by passing a hot current of pure dry air over the sample, see method on page 1041), a few drops of water are added and the evaporation repeated; no odor should be perceptible, all the hydrofluoric, hydrofluosilicic and sulphurous acids being expelled. The sulphuric acid is cooled, taken up with 100 cc. of  $\text{CO}_2$ -free water, three drops of strong phenolphthalein added and the acid titrated with N/1 NaOH solution in a 50-cc. burette. The cc. titration divided by the weight of the sample is noted as C. (See calculations at the close of the procedure.)

### Sulphurous Acid in Hydrofluoric Acid

Ten grams of the sample are weighed in a tared platinum capsule with cover and washed into a large platinum dish with about 75 cc. of water. N/10 Iodine solution is added to a faint yellow. The end point is made more distinct by addition of a little starch solution near the end of the reaction.

One cc. of N/10 I = 0.0041 g.  $\text{H}_2\text{SO}_3$ . cc. N/10 I + wt. of sample = D.

#### Calculation of Results.

Factors.  $\text{H}_2\text{SO}_4 \times 0.4904 = \text{H}_2\text{SiF}_6$ .

$\text{H}_2\text{SO}_4 \times 0.4080 = \text{HF}$ .

One cc. N/10 I = 0.0041 g.  $\text{H}_2\text{SO}_3$ .

Symbols. A = cc. NaOH for total acidity (cold) + wt. of sample.

B = cc. of NaOH addition for  $\text{H}_2\text{SiF}_6$  (hot) + wt. of sample.

C = cc. NaOH for  $\text{H}_2\text{SO}_4$  + wt. of sample.

D = cc. N/10 iodine + wt. of sample.

**Formulae for Calculation.** If E = value of 1 cc. of the standard N/1 caustic in terms of  $\text{H}_2\text{SO}_4$ , then

$$\text{Per cent HF} = \left( A - \frac{B}{2} - C \right) \times E \times 0.408 \times 100 - 0.2D;$$

$$\text{Per cent H}_2\text{SiF}_6 = \frac{3}{2} B \times E \times 0.4904 \times 100;$$

$$\text{Per cent H}_2\text{SO}_4 = C \times E \times 100;$$

$$\text{Per cent H}_2\text{SO}_3 = D \times 0.0041 \times 100.$$

**Residue.** This is determined by evaporation of 15 to 20 grams of the acid in a platinum dish, and gentle ignition of the dry residue.

**NOTES AND PRECAUTIONS.** Weighings should be made quickly in covered platinum weighing bottles.

The end-point in the cold titration is the first pink that persists for 15 seconds.

It is advisable to weigh out the sample for the sulphuric acid determination first and start the evaporation to facilitate more rapid results.

Iodine is preferred to permanganate for titration of  $\text{H}_2\text{SO}_3$ , as the latter also titrates organic matter that is apt to occur in the acid.

## COMPLETE ANALYSIS OF NITRIC ACID

The acidity of nitric acid obtained by titration with standard caustic may be due not only to  $\text{HNO}_3$  but to impurities  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and lower oxides of nitrogen, hence for extremely accurate analysis it is essential to look for these impurities and make allowances accordingly if they are found to be present. Nitric acid may be determined directly by titration with ferrous sulphate according to the procedure given in detail, page 1024; this titration will include combined nitrates as well as the free acid, whereas the titration with caustic includes only free acids. In addition to the above-mentioned impurities, commercial nitric acid frequently contains free chlorine, chlorides, chlorates, iodine, iodides, iodates, silica, and suspended solids; the last is reported as insoluble residue. In an analysis of nitric acid the impurities, which are known to be injurious to the art for which the acid is used, are looked for and determined if present.

### Determination of Total Acidity

As in case of mixed acids and, in fact, all accurate determinations of acids with caustic, such an amount of the sample should be taken as will require a titration within the limits of the standard chamber burette—75 to 100 cc. For normal caustic this would require 4.726 to 6.3 grams of 100%  $\text{HNO}_3$  or a fifth or tenth of this amount for N/5 or N/10  $\text{NaOH}$ . From the specific gravity of the acid its approximate strength can be obtained by referring to the table for nitric acid and calculating the volume and approximate weight required for analysis (see example under Methods of Weighing Acids—Dilute Acids—Non-Volatile under Ordinary Conditions, page 1011).

The acid is weighed in a weighing bottle, or in the Dely tube or Blay-Burkhard pipette, if it is a fuming acid. The titration is made in a casserole, the acid being mixed with 150 to 200 cc. of  $\text{CO}_2$  free water and titrated in presence of phenolphthalein indicator. (Methyl-orange is destroyed by nitrous acid.) The total acidity is expressed in terms of  $\text{H}_2\text{SO}_4$  if other acids are present.

$\frac{\text{cc. N/1 NaOH} \times .049043 \times 100}{\text{Weight of the sample}} = \text{per cent } \text{H}_2\text{SO}_4 \text{ equivalent. } \text{H}_2\text{SO}_4 \times 1.285 = \text{HNO}_3$

Direct calculation to  $\text{HNO}_3$ ,  $\frac{\text{cc. N/1 NaOH} \times 0.063018 \times 100}{\text{Weight of the sample}} = \text{per cent } \text{HNO}_3$ .

### Determination of Sulphuric Acid in Nitric Acid

About 10 grams of the acid are evaporated to dryness on the steam bath. The residue is taken up with about 10 cc. of water and the evaporation repeated until free from nitric fumes, the residue finally diluted to 100 cc. and the sulphuric acid titrated with N/5  $\text{NaOH}$ , using phenolphthalein or methyl-orange indicator. Gravimetrically the acid may be precipitated from a hot solution as  $\text{BaSO}_4$  by addition of barium chloride reagent according to the method for determining sulphur.

One cc. N/5  $\text{NaOH} = 0.009809$  gram  $\text{H}_2\text{SO}_4$ .

$\text{BaSO}_4 \times 0.4202 = \text{H}_2\text{SO}_4$ . Per cent = 100 divided by weight of sample  $\times \text{H}_2\text{SO}_4$  obtained.

<sup>1</sup> Approximate strength may be ascertained by taking the gravity of the acid and referring to the table following on page 1029.

### Determination of Hydrochloric Acid in Nitric Acid

A 5- to 50-gram sample is taken, that is to say, a sufficient amount of the acid so that a weighable amount of AgCl may be obtained. The sample is nearly neutralized with  $\text{NH}_4\text{OH}$  (it should be slightly acid with  $\text{HNO}_3$ ) and a slight excess of silver nitrate reagent added to the hot solution; the mixture is stirred thoroughly, then allowed to settle for one or two hours. The AgCl is filtered through a weighed Gooch crucible containing an asbestos mat, then washed, dried and ignited at a low red heat. (See general method for the determination of chlorine.)

Factors.  $\text{AgCl} \times 0.2474 = \text{Cl}$ .  $\text{AgCl} \times 0.2544 = \text{HCl}$ .

$\text{AgCl} \times 0.34212 = \text{equivalent } \text{H}_2\text{SO}_4$ .

Find the per cent HCl and the per cent equivalent  $\text{H}_2\text{SO}_4$ .

### Lower Oxides. Determined as Nitrous Acid

For practical purposes the lower oxides of nitrogen that may be present in nitric acid are calculated to  $\text{N}_2\text{O}_3$  or  $\text{HNO}_2$ . If it is desired to report these as  $\text{N}_2\text{O}_3$  the conversion factor given below may be used. The lower oxides may be obtained by titration with standard permanganate, other reducing agents being absent. In presence of organic matter titration with standard iodine solution should be made. (See general procedure for determination of nitrous acid, etc.)

It makes but little difference whether the permanganate is added to the sample containing nitrite or the sample added to a measured amount of permanganate, provided in the first method the titration be made as rapidly as possible to prevent oxidation taking place due to dilution of the sample with water. The end-point in the first procedure is quicker and sharper.

Potassium permanganate oxidizes nitrous acid to nitric according to the reaction  $2\text{KMnO}_4 + 5\text{HNO}_2 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{HNO}_3 + 3\text{H}_2\text{O}$ . Therefore 1 cc. of N/1  $\text{KMnO}_4 = 0.02351$  gram  $\text{HNO}_2$  or 0.019 gram  $\text{N}_2\text{O}_3$ .

Twenty-five cc. of the acid are diluted in a casserole to about 300 cc. with cold water, and 25 cc. of dilute  $\text{H}_2\text{SO}_4$ , 1 : 4 added. The solution is titrated immediately with N/5  $\text{KMnO}_4$ , the reagent being added rapidly at first and finally drop by drop as the end-point is approached. The reaction near the end is apt to be slow, so that time must be allowed for complete oxidation. The titration is completed when a pink color is obtained, that persists for three minutes.

cc. N/5  $\text{KMnO}_4 \times 0.004702 = \text{gram } \text{HNO}_2$ .

The result multiplied by  $\frac{100}{\text{wt. sample}} = \text{per cent}$ .

$\text{HNO}_2 \times 1.0431 = \text{equivalent } \text{H}_2\text{SO}_4$ .

### Nitric Acid

From the total acidity expressed as  $\text{H}_2\text{SO}_4$  is subtracted the acidity due to HCl and  $\text{HNO}_2$  (lower oxides of nitrogen) expressed in terms of  $\text{H}_2\text{SO}_4$ . The remainder is due to nitric acid, in terms of sulphuric acid.

$\text{H}_2\text{SO}_4 \times 1.285 = \text{HNO}_3$ .

### Determination of Iodine in Nitric Acid

Fifty cc. of the acid in an Erlenmeyer flask is neutralized with caustic, the mixture being cooled in running water during the operation. The solution, poured into a separatory funnel, is made acid with dilute  $\text{H}_2\text{SO}_4$  and a few drops of 1% solution of  $\text{KNO}_3$  added, followed by about 25 cc. of  $\text{CS}_2$  or  $\text{CCl}_4$ . The mixture is shaken to extract the free iodine and the  $\text{CS}_2$  or  $\text{CCl}_4$  drawn off and the extraction repeated by addition of  $\text{KNO}_3$  and  $\text{CS}_2$  or  $\text{CCl}_4$  until all the iodine has been extracted. Iodine present as iodide is extracted by this method. To obtain the iodine from iodate,  $\text{H}_2\text{S}$  water is added and the extraction with addition of  $\text{NaNO}_2$  and  $\text{CS}_2$  repeated.

The combined extracts are washed in a separatory funnel until free of acid. The iodine is now titrated with standard sodium thiosulphate by adding 25 to 30 cc. of water together with 5 cc. of 1% sodium bicarbonate solution (10 grams  $\text{NaHCO}_3$  per liter + 1 cc.  $\text{HCl}$ ).

One cc. N/10  $\text{Na}_2\text{S}_2\text{O}_3 = 0.01269$  gram I.

#### Reactions.



### Determination of Free Chlorine in Nitric Acid

When a current of pure air is passed into nitric acid containing free chlorine the air blows out the chlorine. If air aspirated through a sample of nitric acid is passed through a solution of potassium iodide the free chlorine will displace the iodine. The liberated iodine may now be titrated with standard sodium thiosulphate and the equivalent chlorine calculated.

### Total Non-Volatile Solids

These may be determined by evaporating a large sample of 100 to 200 cc. of the nitric acid to dryness. The residue is heated gently to expel the last traces of nitric acid and then washed into a platinum dish, again evaporated to dryness and ignited to a dull red heat. The residue is due to non-volatile solids.

## FERROUS SULPHATE METHOD FOR THE DIRECT DETERMINATION OF NITRIC ACID<sup>1</sup>

Although the test for nitric acid by ferrous sulphate in presence of strong sulphuric acid has long been known, the reagent has not been used for an accurate quantitative method until F. C. Bowman and W. W. Scott, General Chemical Company, developed the procedure herein given. Nitric acid may be determined quantitatively in arsenic acid by titration with ferrous sulphate containing free sulphuric acid. The method is also applicable to the determination of nitric acid in phosphoric acid and in sulphuric acid, including oleums and mixed acids. The reaction in phosphoric acid and arsenic acid goes further than it does in sulphuric acid. The following equations represent the reactions taking place:

Reaction in Arsenic or Phosphoric Acids:



Reaction in Sulphuric Acid:



Oxidizing agents such as chlorates, iodates, bromates, etc., interfere, owing to their oxidizing action on ferrous sulphate, hence these should be absent from the sample or allowance made, if appreciable amounts are present. NaCl up to .002 gram does not interfere; larger amounts tend to lower results. KI and KBr react in a similar manner to NaCl, 0.002 gram causing no interference. KNO<sub>3</sub> present in amounts up to 50% of the HNO<sub>3</sub> does not interfere. The sample should not contain over 25% water, nor should the temperature exceed 60° C. during titration. 0.1 to 0.8 gram HNO<sub>3</sub> are accurately titrated, in sulphuric acid.

**Special Reagents Required. Standard Ferrous Sulphate.**

**A. Reagent to be Used in Titration of Nitric Acid in Sulphuric Acid, Oleum, etc.** 176.5 grams of FeSO<sub>4</sub>·7H<sub>2</sub>O are dissolved in about 400 cc. of water, and 500 cc. of about 60% H<sub>2</sub>SO<sub>4</sub> (1 vol. 66° Bé. acid per 1 vol. H<sub>2</sub>O) are added with constant stirring, and the solution (cooled if necessary) made up to 1000 cc. 1 cc. will be equivalent to 0.02 ± gram HNO<sub>3</sub>, the exact value being determined by standardization.

**B. Reagent for Titration of Nitric in Phosphoric or Arsenic Acid.** Ferrous sulphate to be used, should be made up as follows: 264.7 grams of FeSO<sub>4</sub>·7H<sub>2</sub>O is dissolved in 500 cc. of water, 50 cc. of 66° Bé. H<sub>2</sub>SO<sub>4</sub> (93.2%), added and the solution made up to 1000 cc. 1 cc. will be equal to approximately 0.02 gram HNO<sub>3</sub>. The exact strength is ascertained by titrating a known amount of nitric acid in phosphoric or arsenic acid upon warming to 40° or 50° C.

**Standard Nitric Acid.** The acid should contain about 40 grams of HNO<sub>3</sub> (100%) per liter of solution, e.g., 41 cc. of the desk reagent (sp.gr. 1.42) per liter will give the strength desired, the exact value being determined by titration of the acid against standard caustic.

**Potassium Dichromate, N/2 K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Solution.** The exact value in terms of iron should be known.

<sup>1</sup> The Jour. Ind. Eng. Chem., 7, 766, 1915.

## Standardization of Ferrous Sulphate Reagent

### 1. Titration against standard nitric acid.

#### *A. Reagent to be Used for Determination of Nitric in Sulphuric Acid.*

10 cc. of the standard  $\text{HNO}_3 = 0.4 \pm$  g. (the exact amount having been ascertained), is run into 100 cc. of 66° B $\acute{e}$ . (93.2%)  $\text{H}_2\text{SO}_4$ , free from oxidizing agents ( $\text{HNO}_3$ , etc.) and the resulting mixture titrated with the standard  $\text{FeSO}_4$  solution according to the directions given under the General Procedure for determining  $\text{HNO}_3$  in  $\text{H}_2\text{SO}_4$ , page 1026.

Weight of  $\text{HNO}_3$  taken divided by cc. of  $\text{FeSO}_4$  minus 0.2 cc. <sup>1</sup> = grams  $\text{HNO}_3$  per cc.  $\text{FeSO}_4$ .

*B. Standardization of the Reagent Used in the Determination of Nitric in Arsenic and Phosphoric Acids.* 10 cc. of the standard  $\text{HNO}_3 = 0.4 \pm$  gram (the exact amount having been ascertained) is run into 100 cc. of  $\text{H}_3\text{AsO}_4$ , or  $\text{H}_3\text{PO}_4$ , according to the product to be titrated, the mixture warmed and titrated according to directions given under Procedure for determination of  $\text{HNO}_3$  in arsenic or phosphoric acid.

Weight of  $\text{HNO}_3$  taken, divided by cc.  $\text{FeSO}_4$  = grams  $\text{HNO}_3$  per cc.  $\text{FeSO}_4$ .

### 2. Standardizing Ferrous Sulphate with Standard Potassium Dichromate.

#### *A. Reagent to be Used in Determination of Nitric in Sulphuric Acid.*

25 cc. of  $\text{N}/2 \text{ K}_2\text{Cr}_2\text{O}_7$  (or 125 cc.  $\text{N}/10 \text{ K}_2\text{Cr}_2\text{O}_7$ ), are accurately measured out into a 250-cc. beaker and the solution titrated with the  $\text{FeSO}_4$  reagent, until the first fraction of a drop of excess produces a blue color with potassium ferricyanide indicator on a spot plate. Usually between 19 to 20 cc. are required. The iron value of the dichromate multiplied by 0.5643 = gram  $\text{HNO}_3$  for the total cc. of  $\text{FeSO}_4$  required in the titration.

Calculation.

Since  $\text{N}/2 \text{ K}_2\text{Cr}_2\text{O}_7 = 0.024517$  gram salt, 1 gram  $\text{K}_2\text{Cr}_2\text{O}_7 = 1.13882 \text{ Fe}$ , therefore 25 cc. =  $0.024517 \times 1.13882 \times 0.5643 \times 25 = 0.3939$  gram  $\text{HNO}_3$  equivalent.

0.3939 divided by cc.  $\text{FeSO}_4$  required in the titration = grams  $\text{HNO}_3$  equivalent per cc.

*B. Reagent to be Used in Determination of  $\text{HNO}_3$  in  $\text{H}_3\text{AsO}_4$  or  $\text{H}_3\text{PO}_4$ .* 38 cc. of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution are titrated with  $\text{FeSO}_4$  according to directions given in "A". The Fe value multiplied by 0.3762 = gram  $\text{HNO}_3$ .

Calculation. 38 cc. of  $\text{K}_2\text{Cr}_2\text{O}_7 = 0.024517 \times 1.13882 \times 0.3762 \times 38 = 0.3991$  gram  $\text{HNO}_3$  equivalent. 0.3991 divided by cc.  $\text{FeSO}_4$  required in the titration = grams  $\text{HNO}_3$  equivalent per c.c.

Factors.

$\text{K}_2\text{Cr}_2\text{O}_7$  to  $\text{Fe} = 1.13882$ , reciprocal = 0.8781.

$2\text{Fe}$  to  $\text{HNO}_3 = 0.5643$ , recip. = 1.7722.  $3\text{Fe}$  to  $\text{HNO}_3 = 0.3762$ , recip. = 2.6582.

$\text{HNO}_3$  to  $2\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 8.8235$  recip. = 0.1133.

$\text{HNO}_3$  to  $3\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 13.2348$ , recip. = 0.07556.

$\text{K}_2\text{Cr}_2\text{O}_7$  to  $\text{HNO}_3 = 0.6426$ , recip. = 1.5562. (Titration of A reagent.)

$\text{K}_2\text{Cr}_2\text{O}_7$  to  $\text{HNO}_3 = 0.4284$ , recip. = 2.3342. (Titration of B reagent.)

<sup>1</sup>An excess of 0.2 cc.  $\text{FeSO}_4$  is required to produce the desired color reaction in 100 cc. of pure  $\text{H}_2\text{SO}_4$ .

### General Procedure. Determination of Nitric Acid in Sulphuric Acid.

The procedure is applicable to the determination of nitric acid, free or combined as nitrate, sulphuric acid being used as the medium in which the titration is made. Although 0.1 to 0.8 gram  $\text{HNO}_3$  may be accurately titrated, it is a general practice to have the nitric acid content of the sample taken for the titration about the same as the amount taken in standardization of the  $\text{FeSO}_4$  reagent. A preliminary run on the original material is made, if the approximate nitric acid content is not known. Solids are dissolved in water and made to the desired volume, strong  $\text{HNO}_3$  is diluted with water, in either case the dilution should be such that 10 cc. of the solution will contain approximately 0.4 gram  $\text{HNO}_3$ . Mixed acids and oleum containing over 10%  $\text{HNO}_3$  should be mixed with additional 66° B $\acute{\text{e}}$ . (93+ per cent  $\text{H}_2\text{SO}_4$ ) and made to a definite volume, an aliquot part being taken for titration.

### Evaluation of Nitric Acid or Nitrates

If the nitric acid is known to be free of other acids it may be titrated directly with caustic; combined nitrate cannot be titrated with caustic, but may be accurately determined by the ferrous sulphate method. The approximate strength of the  $\text{HNO}_3$  or salt having been determined on 1 cc. or 1 gram sample (if the material is a solid), the requisite amount is weighed and made to volume, 10 cc. of which should contain not more than 0.8 gram or less than 0.1 gram  $\text{HNO}_3$ , preferably about 0.4 gram.

**Example.** Suppose 1 cc. required a titration of 43.8 cc.  $\text{FeSO}_4$ , 10 cc. would require a titration of 438 cc., whereas 20 cc. is desired. 438 divided by 20 = approximately 22, e.g., the dilution should be to 22 volumes. 23 cc. of the solution diluted to 500 cc. will give a mixture of the desired strength. 23 cc. are accordingly weighed in a weighing bottle, the acid washed into a beaker transferred then to the graduated 500-cc. flask and made to volume. The preliminary run may be made in two or three minutes.

**Titration.** A 250-cc. beaker containing 100 cc. of strong, nitric free,  $\text{H}_2\text{SO}_4$  (93+%) is placed in a large casserole or deep porcelain dish containing cold water. 10 cc. of the sample are measured out in an accurately marked pipette, graduated to contain exactly 10 cc. The solution is run under the surface of the sulphuric acid, the delivery tip of the pipette being kept in constant circular motion to prevent too much local heating. Since the sides of the beaker are cooled, the tip of the pipette should be kept against the sides in the circular sweep during the delivery. By this procedure loss of nitric acid is reduced to the minimum.

The ferrous sulphate solution is now added from a burette in a fine stream until the yellow color that first forms takes on a faint brownish tinge (dirty yellow). The pipette is now rinsed out by sucking up the mixture and draining it back into the beaker. The titration is now completed, adding the  $\text{FeSO}_4$  cautiously drop by drop until the yellowish brown color again appears, a drop in excess producing an appreciable darkening of the solution. A larger excess produces a brownish red color. With small amounts of  $\text{HNO}_3$  a pink color will be obtained, instead of the yellowish brown. The end-point once recognized is readily duplicated.

**Calculation.** The cc. titration minus the blank 0.2 cc. multiplied by the factor for  $\text{FeSO}_4$  = weight of  $\text{HNO}_3$ .  $\text{HNO}_3 \times 100 \div \text{wt.} = \text{per cent.}$

**Example.** Suppose 10 cc. equivalent to 1/50 of a 42-g. sample weighed, requires 22 cc.  $\text{FeSO}_4$  whose value = 0.02 g.  $\text{HNO}_3$  per cc., then  $(0.44 \times 100)/0.84 = 52.4\% \text{ HNO}_3$ .

### Determination of Nitric Acid in Oleum or in Mixed Acids. Ferrous Sulphate Method

The rapidity and accuracy of the method for determining  $\text{HNO}_3$  in sulphuric acid makes it valuable for determining nitric acid in oleums and mixed acids. Nitrated oleums may be weighed and titrated without diluting to definite volume, mixed acids containing large percentages of nitric acid, however, require dilution with  $\text{H}_2\text{SO}_4$ , as stated under General Procedure.

**Procedure.** The sample may be weighed in a Dely weighing tube (see analysis of oleum and mixed acids), or in a standard pipette (5 cc. generally taken = 9.61 grams). If the latter is used, the sample is sucked into the pipette, a rubber tube, with glass bead valve, being attached to the upper end, to which suction is applied without danger of drawing  $\text{SO}_2$  fumes into the mouth. A little vaseline placed on the tip of the pipette prevents loss of acid during the weighing. In routine analysis, where a large number of daily samples of oleum are analyzed, and the specific gravity of the oleum does not vary appreciably, 5- to 10-cc. samples may be drawn out, by means of a pipette, and titrated without weighing, the weight being calculated from the gravity.

The acid is run under cold concentrated  $\text{H}_2\text{SO}_4$  (93%), and titrated according to directions under General Procedure for Nitric acid. A blank of 0.2 cc.<sup>1</sup> having been deducted, cc.  $\text{FeSO}_4 \times \text{HNO}_3$  factor for  $\text{FeSO}_4 \times 100$  divided by wt. taken = per cent  $\text{HNO}_3$ .

**Correction Factor.** In making a number of runs with varying amounts of  $\text{HNO}_3$ , it was found that small quantities of nitric acid required a proportional greater amount of  $\text{FeSO}_4$  than larger quantities of  $\text{HNO}_3$ . For example, 0.07392 gram  $\text{HNO}_3$  required 3.9 cc.  $\text{FeSO}_4$ , four times the amount of  $\text{HNO}_3$  required 15 cc.  $\text{FeSO}_4$ , in place of 15.6, ( $3.9 \times 4$ ) and six times 0.07392 gram  $\text{HNO}_3$  required 22.5 cc.  $\text{FeSO}_4$  in place of 23.4. It was observed that even traces of  $\text{HNO}_3$  required a titration of over 0.2 cc. It is evident that a deduction of 0.2 cc. makes the titrations multiples of the lowest, e.g., 3.7, 14.8 and 22.3. Again it was found that standardization of  $\text{FeSO}_4$  with  $\text{HNO}_3$  checked the dichromate factor when 0.2 cc. was deducted from the first series of titrations. This led to the conclusion that a constant blank of 0.2 cc. should be deducted from the ferrous sulphate titrations of nitric acid in presence of 100 cc. of nitric free sulphuric acid, (66° B $\phi$ ).

**Comparison of results:**

$\text{FeSO}_4$  value by  $\text{HNO}_3$  corrected = 0.02067 gram. Uncorrected = 0.02045 gram  $\text{HNO}_3$ .

$\text{FeSO}_4$  value by  $\text{K}_2\text{Cr}_2\text{O}_7$  titration = 0.02083 gram  $\text{HNO}_3$ .

**Accuracy of the Ferrous Sulphate Method.** Results obtained by the ferrous sulphate method agree closely with those obtained by the nitrometer. The following data were obtained by Mr. B. S. Clark,<sup>1</sup> by the  $\text{FeSO}_4$  method, on nitrated oleums. The figures below the first row are checks obtained on these samples by purchasers of the acid, the nitrometer method being used.

$\text{FeSO}_4$ method.	2.40; 2.82; 3.23; 3.35; 3.52; 3.50; 3.48; 3.57; 3.53; 3.56.
Nitrometer method.	2.35; 2.79; 3.26; 3.39; 3.57; 3.53; 3.50; 3.58; 3.57; 3.56.
Difference.	0.05; 0.03; 0.03; 0.04; 0.05; 0.03; 0.02; 0.01; 0.04; 0.00.

<sup>1</sup> Back titrations of the excess of  $\text{FeSO}_4$  may be made with standard  $\text{K}_2\text{Cr}_2\text{O}_7$ , using the ferricyanide spot test for ferrous iron.

Sp.gr. of twelve average samples of oleum had a difference of only 0.01. 5 cc. weighs 9.61 grams. This is found convenient for analysis. 10 cc. = 19.22 grams will usually give a titration of about 20+cc. on the usual nitrated oleum.



### Determination of Nitric Acid in Arsenic and Phosphoric Acids by the Ferrous Sulphate Method

A direct procedure for the determination of nitric acid in arsenic acid or phosphoric acid has been sought on account of the inaccuracy of the evaporation method, since it is difficult to completely expel  $\text{HNO}_3$  from these acids. Ferrous sulphate, in presence of sulphuric acid, quantitatively titrates nitric in arsenic acid, the following reaction taking place:



The procedure is applicable to the determination of nitric acid in phosphoric acid, the end-point being sharper in this acid than in arsenic. The procedure gives very excellent results in either acid and is recommended for accuracy and rapidity.

**Standardization of Ferrous Sulphate** has already been given under special reagents. It must be remembered that the arsenic or phosphoric acid diluents should be free from nitric acid or the blank on 100 cc. be ascertained and deducted from titrations made in this diluent.

**Procedure.** The amount of the sample to be taken is governed by the nitric acid present as an impurity. This may be quickly determined by a preliminary run on a 10-cc. sample, the diluent being the same acid ( $\text{HNO}_3$  free) as the acid titrated.

**Example.** Suppose 10 cc. require a titration of 4.5 cc. of  $\text{FeSO}_4$ , whereas a titration of 20 cc. is desired, then  $20 \times 10 \div 4.5 = 44.44$  cc. of the sample required.

The required amount of the acid is measured out and weighed, if its sp.gr. is not known. The acid is poured into a 4-in. casserole and diluted with 100 cc. of nitric free acid of the same kind as that being titrated. The mixture is gently warmed to 40 to 50° C. and titrated with standard ferrous sulphate reagent to a permanent yellowish brown. Towards the end of the titration the acid will boil with each addition of the  $\text{FeSO}_4$  and the characteristic reddish yellow fumes will be given off. (This does not occur in titrations of  $\text{HNO}_3$  in  $\text{H}_2\text{SO}_4$ .)

When very small amounts of nitric acid are present it is often necessary to add a known amount of  $\text{HNO}_3$  to start the reaction. The titration in excess of that required by the added  $\text{HNO}_3$  is due to the nitric acid in the sample. Very small amounts of  $\text{HNO}_3$  produce a pink color.

Calculation cc.  $\text{FeSO}_4 \times \text{HNO}_3$  factor for  $\text{FeSO}_4 \times 100$  divided by weight taken = per cent  $\text{HNO}_3$ .

**Factors.** Fe to  $\text{HNO}_3 = 0.3762$ . Reciprocal = 2.6582.

**NOTE.** In a 20-gram sample 1 cc. 0.02 reagent = 0.1% per cc.

### DETERMINATION OF NITROUS ACID OR NITRITE PERMANGANATE METHOD

**Principle.** Potassium permanganate reacts with nitrous acid or a nitrite as follows:



Details of the general procedure for nitrites is given on page 358, Vol. I. Nitrous acid in nitric acid may be determined as stated on page 1022. Lower oxides of nitrogen in mixed acids are determined as outlined on page 1042.

NITRIC ACID  
By W. C. FERGUSON

Degrees Baumé.	Sp. Gr. 60° F.	Degrees Twaddell.	Per Cent HNO <sub>3</sub> .	Degrees Baumé.	Sp. Gr. 60° F.	Degrees Twaddell.	Per Cent HNO <sub>3</sub> .
10.00	1.0741	14.82	12.86	21.25	1.1718	34.36	28.02
10.25	1.0761	15.22	13.18	21.50	1.1741	34.82	28.21
10.50	1.0781	15.62	13.49	21.75	1.1765	35.30	28.72
10.75	1.0801	16.02	13.81	22.00	1.1789	35.78	29.07
11.00	1.0821	16.42	14.13	22.25	1.1813	36.26	29.43
11.25	1.0841	16.82	14.44	22.50	1.1837	36.74	29.78
11.50	1.0861	17.22	14.76	22.75	1.1861	37.22	30.14
11.75	1.0881	17.62	15.07	23.00	1.1885	37.70	30.49
12.00	1.0902	18.04	15.41	23.25	1.1910	38.20	30.86
12.25	1.0922	18.44	15.72	23.50	1.1934	38.68	31.21
12.50	1.0943	18.86	16.05	23.75	1.1959	39.18	31.58
12.75	1.0964	19.28	16.39	24.00	1.1983	39.68	31.94
13.00	1.0985	19.70	16.72	24.25	1.2008	40.16	32.31
13.25	1.1006	20.12	17.05	24.50	1.2033	40.66	32.68
13.50	1.1027	20.54	17.38	24.75	1.2058	41.16	33.05
13.75	1.1048	20.96	17.71	25.00	1.2083	41.66	33.42
14.00	1.1069	21.38	18.04	25.25	1.2109	42.18	33.80
14.25	1.1090	21.80	18.37	25.50	1.2134	42.68	34.17
14.50	1.1111	22.22	18.70	25.75	1.2160	43.20	34.56
14.75	1.1132	22.64	19.02	26.00	1.2185	43.70	34.94
15.00	1.1154	23.08	19.36	26.25	1.2211	44.22	35.33
15.25	1.1176	23.52	19.70	26.50	1.2236	44.72	35.70
15.50	1.1197	23.94	20.02	26.75	1.2262	45.24	36.09
15.75	1.1219	24.38	20.36	27.00	1.2288	45.76	36.48
16.00	1.1240	24.80	20.69	27.25	1.2314	46.28	36.87
16.25	1.1262	25.24	21.03	27.50	1.2340	46.80	37.26
16.50	1.1284	25.68	21.36	27.75	1.2367	47.34	37.67
16.75	1.1306	26.12	21.70	28.00	1.2393	47.86	38.08
17.00	1.1328	26.56	22.04	28.25	1.2420	48.40	38.46
17.25	1.1350	27.00	22.38	28.50	1.2446	48.92	38.85
17.50	1.1373	27.46	22.71	28.75	1.2473	49.46	39.25
17.75	1.1395	27.90	23.08	29.00	1.2500	50.00	39.66
18.00	1.1417	28.34	23.42	29.25	1.2527	50.54	40.06
18.25	1.1440	28.80	23.77	29.50	1.2554	51.08	40.47
18.50	1.1462	29.24	24.11	29.75	1.2582	51.64	40.89
18.75	1.1485	29.70	24.47	30.00	1.2609	52.18	41.30
19.00	1.1508	30.16	24.82	30.25	1.2637	52.74	41.72
19.25	1.1531	30.62	25.18	30.50	1.2664	53.28	42.14
19.50	1.1554	31.08	25.53	30.75	1.2692	53.84	42.58
19.75	1.1577	31.54	25.88	31.00	1.2719	54.38	43.00
20.00	1.1600	32.00	26.24	31.25	1.2747	54.94	43.44
20.25	1.1624	32.48	26.61	31.50	1.2775	55.50	43.89
20.50	1.1647	32.94	26.96	31.75	1.2804	56.08	44.34
20.75	1.1671	33.42	27.33	32.00	1.2832	56.64	44.78
21.00	1.1694	33.90	27.67	32.25	1.2861	57.22	45.24

## NITRIC ACID (Continued)

Degrees Baumé.	Sp. Gr. 60° F.	Degrees Twaddell.	Per Cent HNO <sub>3</sub> .	Degrees Baumé.	Sp. Gr. 60° F.	Degrees Twaddell.	Per Cent HNO <sub>3</sub> .
32.50	1.2889	57.78	45.68	40.75	1.3909	78.18	63.48
32.75	1.2918	58.36	46.14	41.00	1.3942	78.84	64.20
33.00	1.2946	58.92	46.58	41.25	1.3976	79.52	64.93
33.25	1.2975	59.50	47.04	41.50	1.4010	80.20	65.67
33.50	1.3004	60.08	47.49	41.75	1.4044	80.88	66.42
33.75	1.3034	60.68	47.95	42.00	1.4078	81.56	67.18
34.00	1.3063	61.26	48.42	42.25	1.4112	82.24	67.95
34.25	1.3093	61.86	48.90	42.50	1.4146	82.92	68.73
34.50	1.3122	62.44	49.35	42.75	1.4181	83.62	69.52
34.75	1.3152	63.04	49.83	43.00	1.4216	84.32	70.33
35.00	1.3182	63.64	50.32	43.25	1.4251	85.02	71.15
35.25	1.3212	64.24	50.81	43.50	1.4286	85.72	71.98
35.50	1.3242	64.84	51.30	43.75	1.4321	86.42	72.82
35.75	1.3273	65.46	51.80	44.00	1.4356	87.12	73.67
36.00	1.3303	66.06	52.30	44.25	1.4392	87.84	74.53
36.25	1.3334	66.68	52.81	44.50	1.4428	88.56	75.40
36.50	1.3364	67.28	53.32	44.75	1.4464	89.28	76.28
36.75	1.3395	67.90	53.84	45.00	1.4500	90.00	77.17
37.00	1.3426	68.52	54.36	45.25	1.4536	90.72	78.07
37.25	1.3457	69.14	54.89	45.50	1.4573	91.46	79.03
37.50	1.3488	69.76	55.43	45.75	1.4610	92.20	80.04
37.75	1.3520	70.40	55.97	46.00	1.4646	92.92	81.08
38.00	1.3551	71.02	56.52	46.25	1.4684	93.68	82.18
38.25	1.3583	71.66	57.08	46.50	1.4721	94.42	83.33
38.50	1.3615	72.30	57.65	46.75	1.4758	95.16	84.48
38.75	1.3647	72.94	58.23	47.00	1.4796	95.92	85.70
39.00	1.3679	73.58	58.82	47.25	1.4834	96.68	86.98
39.25	1.3712	74.24	59.43	47.50	1.4872	97.44	88.30
39.50	1.3744	74.88	60.06	47.75	1.4910	98.20	89.76
39.75	1.3777	75.54	60.71	48.00	1.4948	98.96	91.35
40.00	1.3810	76.20	61.38	48.25	1.4987	99.74	93.13
40.25	1.3843	76.86	62.07	48.50	1.5026	100.52	95.11
40.50	1.3876	77.52	62.77				

Specific Gravity determinations were made at 60° F., compared with water at 60° F.  
From the Specific Gravities, the corresponding degrees Baumé were calculated by the following formula:

$$\text{Baumé} = 145 - \frac{145}{\text{Sp. Gr.}}$$

Baumé Hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

## ALLOWANCE FOR TEMPERATURE:

At 10° — 20°	Bé. — 1/30° Bé. or .00029 Sp. Gr. = 1° F.
20° — 30°	Bé. — 1/23° Bé. or .00044 " " = 1° F.
30° — 40°	Bé. — 1/20° Bé. or .00060 " " = 1° F.
40° — 48.5°	Bé. — 1/17° Bé. or .00084 " " = 1° F.

AUTHORITY — W. C. FERGUSON.

This table has been approved and adopted as a Standard by the Manufacturing Chemists' Association of the United States.

New York, May 14, 1903.

W. H. BOWER, JAS. L. MORGAN,  
HENRY HOWARD, ARTHUR WYMAN,  
A. G. ROSENGARTEN, Executive Committee

NITRIC ACID  
LUNGE AND REY

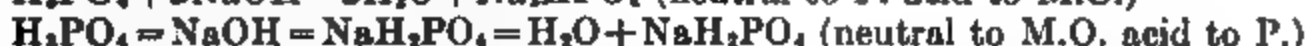
Specific Gravity 15° 4° in vacuo	100 parts by weight contain		1 liter contains grams		Specific Gravity 15° 4° in vacuo	100 parts by weight contain		1 liter contains grams	
	% N <sub>2</sub> O <sub>5</sub>	% HNO <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>		% N <sub>2</sub> O <sub>5</sub>	% HNO <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>
1.000	0.08	0.10	1	1	1.195	27.10	31.62	324	378
1.005	0.85	1.00	8	10	1.200	27.74	32.36	333	388
1.010	1.62	1.90	16	19	1.205	28.36	33.09	342	399
1.015	2.39	2.80	24	28	1.210	28.99	33.82	351	409
1.020	3.17	3.70	33	38	1.215	29.61	34.55	360	420
1.025	3.94	4.60	40	47	1.220	30.24	35.28	369	430
1.030	4.71	5.50	49	57	1.225	30.88	36.03	378	441
1.035	5.47	6.38	57	66	1.230	31.53	36.78	387	452
1.040	6.22	7.26	64	75	1.235	32.17	37.53	397	463
1.045	6.97	8.13	73	85	1.240	32.82	38.29	407	475
1.050	7.71	8.99	81	94	1.245	33.47	39.05	417	486
1.055	8.43	9.84	89	104	1.250	34.13	39.82	427	498
1.060	9.15	10.68	97	113	1.255	34.78	40.58	437	509
1.065	9.87	11.51	105	123	1.260	35.44	41.34	447	521
1.070	10.57	12.33	113	132	1.265	36.09	42.10	457	533
1.075	11.27	13.15	121	141	1.270	36.75	42.87	467	544
1.080	11.96	13.95	129	151	1.275	37.41	43.64	477	556
1.085	12.64	14.74	137	160	1.280	38.07	44.41	487	568
1.090	13.31	15.53	145	170	1.285	38.73	45.18	498	581
1.095	13.99	16.32	153	179	1.290	39.39	45.95	508	593
1.100	14.67	17.11	161	188	1.295	40.05	46.72	519	605
1.105	15.34	17.89	170	198	1.300	40.71	47.49	529	617
1.110	16.00	18.67	177	207	1.305	41.37	48.26	540	630
1.115	16.67	19.45	186	217	1.310	42.06	49.07	551	643
1.120	17.34	20.23	195	227	1.315	42.76	49.89	562	656
1.125	18.00	21.00	202	236	1.320	43.47	50.71	573	669
1.130	18.66	21.77	211	246	1.325	44.17	51.53	585	683
1.135	19.32	22.54	219	256	1.330	44.89	52.37	597	697
1.140	19.98	23.31	228	266	1.3325	45.26	52.80	603	704
1.145	20.64	24.08	237	276	1.335	45.62	53.22	609	710
1.150	21.29	24.84	245	286	1.340	46.35	54.07	621	725
1.155	21.94	25.60	254	296	1.345	47.08	54.93	633	739
1.160	22.60	26.36	262	306	1.350	47.82	55.79	645	753
1.165	23.25	27.12	271	316	1.355	48.57	56.66	658	768
1.170	23.90	27.88	279	326	1.360	49.35	57.57	671	783
1.175	24.54	28.63	288	336	1.365	50.13	58.48	684	798
1.180	25.18	29.38	297	347	1.370	50.91	59.39	698	814
1.185	25.83	30.13	306	357	1.375	51.69	60.30	711	829
1.190	26.47	30.88	315	367	1.380	52.52	61.27	725	846

## NITRIC ACID (Continued)

Specific Gravity 15° 4° in vacuo	100 parts by weight contain		1 liter con- tains grams		Specific Gravity 15° 4° in vacuo	100 parts by weight contain		1 liter con- tains grams	
	% N <sub>2</sub> O <sub>5</sub>	% HNO <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>		% N <sub>2</sub> O <sub>5</sub>	% HNO <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>
1.3833	53.08	61.92	745	857	1.495	78.52	91.60	1174	1369
1.385	53.35	62.24	739	862	1.500	80.65	94.09	1210	1411
1.390	54.20	63.23	753	879	1.501	81.09	94.60	1217	1420
1.395	55.07	64.25	768	896	1.502	81.50	95.08	1224	1428
1.400	55.97	65.30	783	914	1.503	81.91	95.55	1231	1436
1.405	56.92	66.40	800	933	1.504	82.29	96.00	1238	1444
1.410	57.86	67.50	817	952	1.505	82.63	96.49	1244	1451
1.415	58.83	68.63	832	971	1.506	82.94	96.76	1249	1457
1.420	59.83	69.80	849	991	1.507	83.24	97.13	1255	1464
1.425	60.84	70.98	867	1011	1.508	83.58	97.50	1260	1470
1.430	61.86	72.17	885	1032	1.509	83.87	97.84	1265	1476
1.435	62.91	73.39	903	1053	1.510	84.09	98.10	1270	1481
1.440	64.01	74.68	921	1075	1.511	84.28	98.32	1274	1486
1.445	65.13	75.98	941	1098	1.512	84.46	98.53	1277	1490
1.450	66.24	77.28	961	1121	1.513	84.63	98.73	1280	1494
1.455	67.38	78.60	981	1144	1.514	84.78	98.90	1283	1497
1.460	68.56	79.98	1001	1168	1.515	84.92	99.07	1287	1501
1.465	69.79	81.42	1021	1193	1.516	85.04	99.21	1290	1504
1.470	71.06	82.90	1045	1219	1.517	85.15	99.34	1292	1507
1.475	72.39	84.45	1069	1246	1.518	85.26	99.46	1294	1510
1.480	73.76	86.05	1092	1274	1.519	85.35	99.57	1296	1512
1.485	75.18	87.70	1116	1302	1.520	85.44	99.67	1299	1515
1.490	76.80	89.60	1144	1335					

## VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID AND ITS SALTS (METHOD OF SMITH)

In titrating free phosphoric acid it must be borne in mind that  $\text{NaH}_2\text{PO}_4$  reacts acid to phenolphthalein and neutral to methyl orange, while  $\text{Na}_2\text{HPO}_4$  is neutral to phenolphthalein and basic to methyl orange. The reactions are shown as follows:



J. H. Smith outlines the following process for analysis of phosphoric acid free and combined:

**Procedure.** Take five or six grams of the material and dissolve in the minimum quantity of distilled water. Add two drops of phenolphthalein. If the solution is not colored pink by the indicator the absence of trisodium phosphate ( $\text{Na}_3\text{PO}_4$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) may be assumed. Heat to  $55^\circ \text{C.}$  and titrate with N/1 NaOH to the characteristic pink endpoint, being particularly careful to keep the temperature at  $55^\circ \text{C.}$  when near the endpoint. This precaution should be observed in all the titrations as the temperature governs the accuracy of the titrations (see paper by Smith).

Record this titration as "A" and the cc. NaOH required as (a).

The solution is now titrated back with N/1 HCl, using a few drops of methyl orange as indicator, to the pink endpoint.

Record this titration as "B" and the cc. acid required as (b).

**Calculation of the Composition.** If the solution contains only  $\text{Na}_2\text{HPO}_4$  +  $\text{NaH}_2\text{PO}_4$  or  $\text{NaH}_2\text{PO}_4$  +  $\text{H}_3\text{PO}_4$  or only one of these compounds we may assume the following:

If (a) is greater than (b)

$$(a) - (b) = \text{cc. equivalent of N/1 H}_3\text{PO}_4$$

$$(b) = \text{cc. equivalent of N/1 NaH}_2\text{PO}_4$$

If (b) is greater than (a)

$$(b) - (a) = \text{Na}_2\text{HPO}_4$$

$$(a) = \text{NaH}_2\text{PO}_4$$

If (a) = (b)

Each titration =  $\text{NaH}_2\text{PO}_4$  present.

If (a) = 2(b)

Only  $\text{H}_3\text{PO}_4$  is present.

**To Ascertain the Presence of Other Salts.** Add N/1 HCl (cc. HCl the same as cc. in titration B). Call this (b'). Boil for at least 15 minutes. By this procedure metaphosphoric acid or its salts is converted to the orthophosphate form, alkaline salts containing carbonates are destroyed and  $\text{CO}_2$  evolved. Cool the solution to  $55^\circ \text{C.}$  and titrate back with N/1 NaOH first to "B" point in which (b'') cc. of alkali is used, and finally to third endpoint (C), where the phenolphthalein pink color is reached. The cc. N/1 NaOH required is recorded as (c).

In titrating back after boiling, the (b'') amount of alkali required to reach the methyl orange point where the pink coloration just appears should always be the same amount as the (b') excess of acid added for boiling (except in the case of polyphosphates being present—see paper). A slight loss of HCl during boiling may cause (b'') to be less than (b'). In any case it is preferable to consider the point reached after addition of the (b'') quantity of alkali as the identical point with B, so that (b') and (b'') are not used in the calculation, but simply employed as a comparative check on each other.

<sup>1</sup> J. H. Smith, Soc. Chem. Ind., 36, 415 (1917).

If the "C" point coincides with the "A" point, i.e., if  $(c) = (b)$  metaphosphoric acid and its salts as well as carbonates in the original substance are excluded.

If  $(c)$  is greater than  $(b)$  the presence of metaphosphates is indicated.

If  $(c)$  is less than  $(b)$  carbonates are evidently present.

With the aid of the three fixed points "A," "B," "C" and the amounts of acid or alkali required to reach them, i.e.,  $(a)$ ,  $(b)$  and  $(c)$  it is possible to calculate the percentages of practically all the phosphoric acids and their salts, which may exist together in a compound, including the carbonates and the free alkali, which may be present with them.

### Calculation of Constituents in a Mixture of Phosphates

If  $(a)$  is greater than  $(b)$

$(a) - (b) = \text{H}_3\text{PO}_4$ ,  $2(b) - (a) = \text{NaH}_2\text{PO}_4$ ,  $(c) - (b) = \text{NaPO}_3$  (generally nil).

If  $(a)$  is greater than  $2(b)$

Then  $(a) - 2(b) =$  measure of metaphosphoric acid or the foreign acid present.

If  $(a)$  is less than  $(b)$

$(a)$  is the measure of  $\text{NaH}_2\text{PO}_4$ ,  $(b) - (a) = \text{Na}_2\text{HPO}_4$ ,

$(c) - (b) = \text{NaPO}_3$  (usually nil).

With alkaline salts "C" coincides with "A," i.e., when no carbonate is present.

If  $(a)$  is less than  $(b)$  then

$(a)$  is a measure of  $\text{Na}_2\text{PO}_4$ ,  $(b) - (a) = \text{Na}_2\text{HPO}_4$ .

Where  $(c)$  is less than  $(b)$ , i.e., when carbonate is present.

If  $(a)$  is less than  $(b)$

$(a) + (c) - (b) = \text{Na}_2\text{PO}_4$ ,  $(b) - (a) = \text{Na}_2\text{HPO}_4$ ,  $(b) - (c) = \text{Na}_2\text{CO}_3$ .

Where no carbonate is present and  $(a)$  is greater than  $(b)$ .

$(b) = \text{Na}_2\text{PO}_4$ ,  $\frac{1}{2}(a - b) = \text{Na}_2\text{O}$ .

Where carbonate is present and  $(a)$  is greater than  $(b)$

$(b) - (c) = \text{Na}_2\text{CO}_3$ ,  $(c) = \text{Na}_2\text{PO}_4$ ,  $\frac{1}{2}(a - b) = \text{Na}_2\text{O}$ .

In calculating the weight of constituents from the above formulae, since normal solutions are used in the titrations each cc. is equivalent to molecular weights divided by 1/1000. In case of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{O}$  the absolute weights are 1/2000 of the respective molecular weights.

Formula	Mol. Wt.	1 cc. Equivalent of Titration	Formula	Mol. Wt.	1 cc. Equivalent of Titration
$\text{H}_3\text{PO}_4$	98.14	0.09814 g.	$\text{NaPO}_3$ . . . .	80.05	0.08005
$\text{NaH}_2\text{PO}_4$	120.05	0.12005	$\text{Na}_2\text{CO}_3$ . . . .	106.01	0.053005
$\text{Na}_2\text{HPO}_4$	142.05	0.14205	$\text{Na}_2\text{O}$ . . . . .	62.00	0.031
$\text{Na}_2\text{PO}_4$	164.04	0.16404			

With water of crystallization  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O} = 138.07$ ,  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} = 156.09$ ,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} = 358.24$ ,  $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O} = 380.23$ ,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} = 286.17$ ,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} = 124.02$ .

NOTES.—In presence of meta or pyro acids and their salts it is well to verify the results with qualitative tests. When pyro acid is present point "A" is obscured and lies much nearer "B," but the correct "A" point is "C" obtained after boiling with the excess acid.

In presence of metaphosphate it is advisable to repeat titrations employing N/1  $\text{H}_2\text{SO}_4$  and evaporating to near dryness to completely convert the meta to ortho compound.

Phosphates attack glass combining with the alkali present. The presence of NaCl obtained in the titrations counteracts this action.

## PHOSPHORIC ACID AT 17.5°

Specific Gravity.	Per Cent. $P_2O_5$ .	Per Cent. $H_2PO_4$ .	Specific Gravity.	Per Cent. $P_2O_5$ .	Per Cent. $H_2PO_4$ .	Specific Gravity.	Per Cent. $P_2O_5$ .	Per Cent. $H_2PO_4$ .
1.809	68.0	93.67	1.462	46.0	63.37	1.208	24.0	31.00
1.800	67.5	92.99	1.455	45.5	62.68	1.203	23.5	32.37
1.792	67.0	92.30	1.448	45.0	61.99	1.198	23.0	31.68
1.783	66.5	91.61	1.441	44.5	61.30	1.193	22.5	30.99
1.775	66.0	90.92	1.435	44.0	60.61	1.188	22.0	30.31
1.766	65.5	90.23	1.428	43.5	59.92	1.183	21.5	29.62
1.758	65.0	89.54	1.422	43.0	59.23	1.178	21.0	28.93
1.750	64.5	88.85	1.415	42.5	58.55	1.174	20.5	28.24
1.741	64.0	88.16	1.409	42.0	57.86	1.169	20.0	27.55
1.733	63.5	87.48	1.402	41.5	57.17	1.164	19.5	26.86
1.725	63.0	86.79	1.396	41.0	56.48	1.159	19.0	26.17
1.717	62.5	86.10	1.389	40.5	55.79	1.155	18.5	25.48
1.709	62.0	85.41	1.383	40.0	55.10	1.150	18.0	24.80
1.701	61.5	84.72	1.377	39.5	54.41	1.145	17.5	24.11
1.693	61.0	84.03	1.371	39.0	53.72	1.140	17.0	23.42
1.685	60.5	83.34	1.365	38.5	53.04	1.135	16.5	22.73
1.677	60.0	82.65	1.359	38.0	52.35	1.130	16.0	22.04
1.669	59.5	81.97	1.354	37.5	51.66	1.126	15.5	21.35
1.661	59.0	81.28	1.348	37.0	50.97	1.122	15.0	20.66
1.653	58.5	80.59	1.342	36.5	50.28	1.118	14.5	19.97
1.645	58.0	79.90	1.336	36.0	49.59	1.113	14.0	19.28
1.637	57.5	79.21	1.330	35.5	48.90	1.109	13.5	18.60
1.629	57.0	78.52	1.325	35.0	48.21	1.104	13.0	17.91
1.621	56.5	77.83	1.319	34.5	47.52	1.100	12.5	17.22
1.613	56.0	77.14	1.314	34.0	46.84	1.096	12.0	16.53
1.605	55.5	76.45	1.308	33.5	46.15	1.091	11.5	15.84
1.597	55.0	75.77	1.303	33.0	45.46	1.087	11.0	15.15
1.589	54.5	75.08	1.298	32.5	44.77	1.083	10.5	14.46
1.581	54.0	74.39	1.292	32.0	44.08	1.079	10.0	13.77
1.574	53.5	73.70	1.287	31.5	43.39	1.074	9.5	13.09
1.566	53.0	73.01	1.281	31.0	42.70	1.070	9.0	12.40
1.559	52.5	72.32	1.276	30.5	42.01	1.066	8.5	11.71
1.551	52.0	71.63	1.271	30.0	41.33	1.062	8.0	11.02
1.543	51.5	70.94	1.265	29.5	40.64	1.058	7.5	10.33
1.536	51.0	70.26	1.260	29.0	39.95	1.053	7.0	9.64
1.528	50.5	69.57	1.255	28.5	39.26	1.049	6.5	8.95
1.521	50.0	68.88	1.249	28.0	38.57	1.045	6.0	8.26
1.513	49.5	68.19	1.244	27.5	37.88	1.041	5.5	7.57
1.505	49.0	67.50	1.239	27.0	37.19	1.037	5.0	6.89
1.498	48.5	66.81	1.233	26.5	36.50	1.033	4.5	6.20
1.491	48.0	66.12	1.228	26.0	35.82	1.029	4.0	5.51
1.484	47.5	65.43	1.223	25.5	35.13	1.025	3.5	4.82
1.476	47.0	64.75	1.218	25.0	34.44	1.021	3.0	4.13
1.469	46.5	64.06	1.213	24.5	33.75	1.017	2.5	3.44



## ANALYSIS OF SULPHURIC ACID

Sulphuric acid made by the contact process is exceedingly pure, the principal impurity being iron, which causes turbidity in strong acid. The acid made by this process is 99% strength. This is diluted to 66° Be (93.19%  $\text{H}_2\text{SO}_4$ ) and is known as oil of vitriol. The acid is also commonly marketed as 60° Be acid (77.67%  $\text{H}_2\text{SO}_4$ ) and 50° Be acid (62.18%  $\text{H}_2\text{SO}_4$ ) obtained by further dilution of the stronger acid. 50° Be acid is also obtained by the chamber process; this acid is not as pure as that produced by the contact process. The impurities occurring in sulphuric acid are iron, lead, copper, zinc, antimony, selenium, arsenic, sulphur dioxide, hydrochloric acid, hydrofluoric acid, nitric acid.

Sulphuric acid up to 93% strength may be determined with a fair degree of accuracy by ascertaining its specific gravity by means of a hydrometer and referring to the tables on sulphuric acid.

Sulphuric acid readily absorbs  $\text{SO}_2$  so that its acidity may be considerably over 100%. This acid, commonly known as oleum, fumes when exposed to the air due to its low vapor tension, the  $\text{SO}_2$  combining with the moisture of the air with formation of  $\text{H}_2\text{SO}_4$  mist.

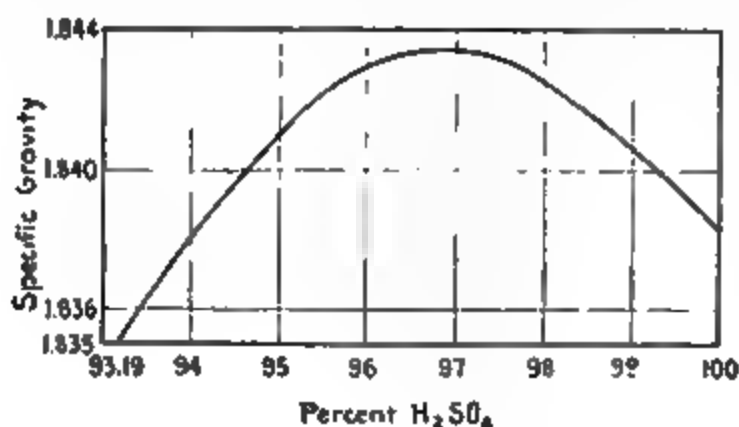


FIG. 81.

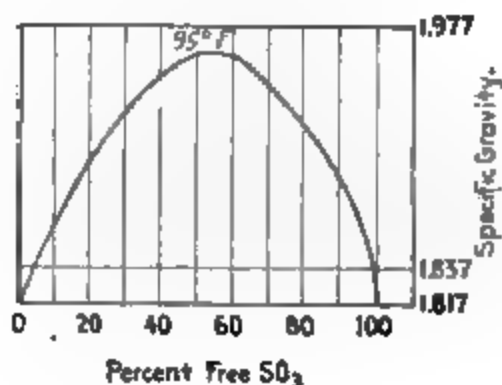


FIG. 82.

Specific Gravity Charts—Sulphuric Acid.

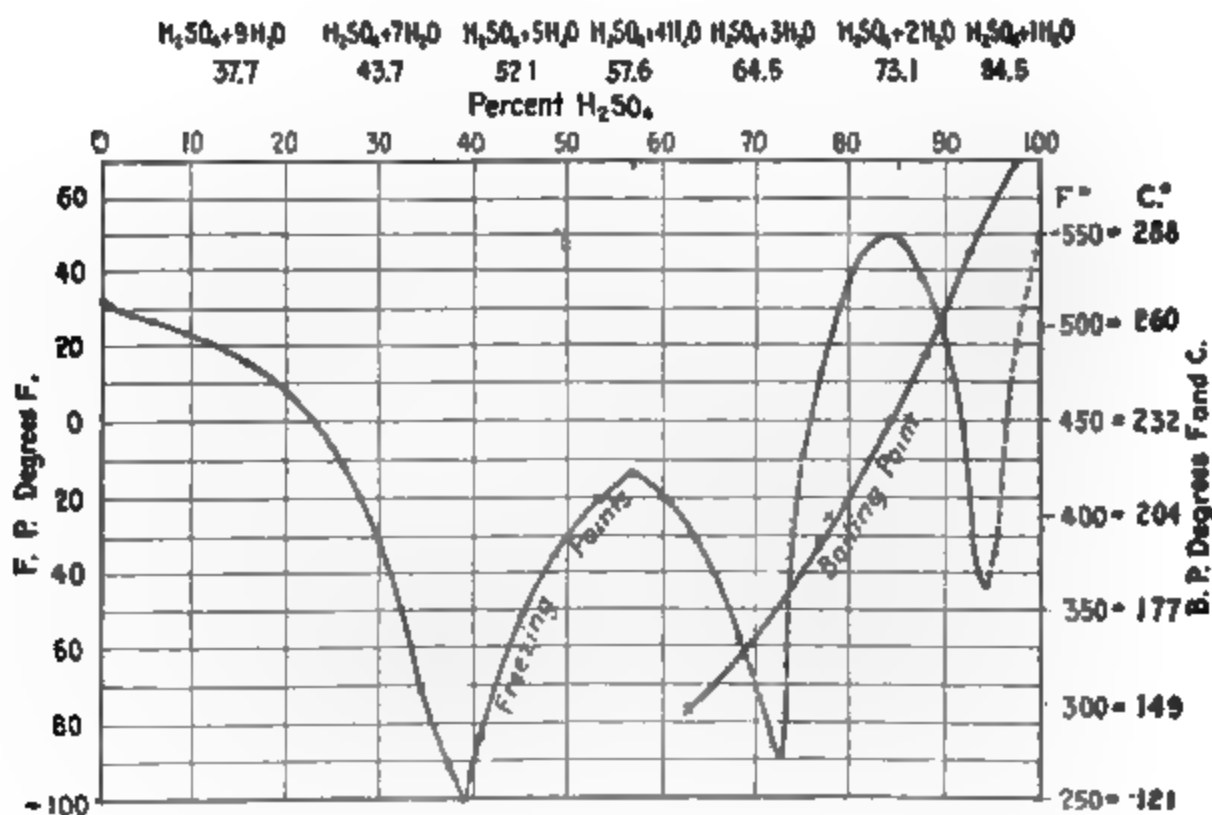


FIG. 83.—Chart Showing Freezing- and Boiling-points of Sulphuric Acid of Varying Concentration.

## SULPHURIC ACID

### Method of Analysis<sup>1</sup>

**Procedure for Titration with Standard NaOH.** Concentrated sulphuric acid absorbs moisture rapidly so that the weighing should be made quickly, the acid having been placed in a special closed receptacle as recommended on pages 1010 to 1012. Such an amount of acid is taken as will require a titration that can be read on the chamber burette used. For example if normal caustic is used and the chamber burette reads from 75 cc. to 100 cc. the acid should contain from 3.7 grams to 4.9 grams of  $H_2SO_4$ . The acid is added to  $CO_2$  free distilled water, preferably in a porcelain casserole, 1 cc. of 1% phenolphthalein added and the titration made to a faint pink color with standard NaOH. It is advisable to titrate the acid using methyl orange if the presence of  $CO_2$  is suspected in the water. Some chemists prefer the use of this indicator. It is a common practice to standardize the acidimetric and alkalimetric reagents in presence of methyl orange and phenolphthalein in separate titrations, recording factors for each.

The temperature of the titrating alkali should be noted and a correction of 0.032 cc. be made for each degree deviation from the temperature at which the reagent was standardized. For each  $1^\circ C.$  that the temperature is above that at standardization subtract this correction, and add this for each degree the temperature is below that at standardization.

$(cc. \text{ titration} \times H_2SO_4 \text{ value per cc.} \times 100) \div \text{wt. of sample} = \% H_2SO_4$ .

### Determination of Impurities in Sulphuric Acid

#### Determination of Residue on Heating

50 to 100 grams of the acid are weighed into a platinum or silica dish and the acid evaporated (Hood) by heating gently over a direct flame. When no more fumes evolve, the dish is cooled and weighed. The increased weight of the dish is due to the residue, composed of substances not volatile at red heat and generally contains iron oxide. Chamber acid may have all of the substances occurring in sulphur ores present in this residue.

#### Determination of Lead

**Minute Amounts.** Determine by means of the colorimeter according to the procedure described on page 281, Vol. I.

**High Lead Contamination.** Larger amounts of lead sulphate may be determined gravimetrically. The lead may be extracted from the residue, obtained on evaporation of the acid and heating, by extracting with ammonium acetate according to the standard procedure, and lead precipitated from the extract made acid with acetic by addition of a small excess of  $K_2Cr_2O_7$  solution. See method on page 274, Vol. I.

If preferred, lead may be determined as follows: 100 grams of the acid are diluted with an equal volume of distilled water and the solution stirred and cooled. Twice the volume of alcohol is added, the lead sulphate allowed to settle for two hours or more and the precipitate filtered on a Gooch crucible the residue washed with alcohol, dried and ignited at dull red heat and weighed as  $PbSO_4$ . If contamination of the lead sulphate is suspected, this residue may be extracted with ammonium acetate and lead precipitated from the extract as  $PbCrO_4$  according to the regular procedure.

$PbCrO_4 \times .641 = Pb.$        $PbSO_4 \times .6331 = Pb.$

<sup>1</sup> Certain details of procedure are published by courtesy of the General Chemical Company.

### Determination of Iron

**Traces of Iron.** The colorimetric procedure is used, iron being determined by color comparison of the thiocyanate with standards. See procedure on page 258, Vol. I. Five grams of the acid are added to 10 cc. of water in a small beaker and the solution heated to dissolve any iron in suspension. The cooled acid is poured into a 100 cc. Nessler tube with rinsing of the beaker. A few drops of N/10  $\text{KMnO}_4$  are added in amount sufficient to obtain a faint pink color, then 10 cc. of a 10% solution of  $\text{NH}_4\text{CNS}$  and the solution made up to 100 cc. Comparison is now made as follows:

The standard is prepared by treating 5 cc. of iron-free sulphuric acid in exactly the same manner as the tested sample, in a separate Nessler tube. Standard iron solution is run in, stirring the solution with a glass plunger, until the color matches that of the sample. It is advisable to make the standard solution to contain 0.00005 g. Fe per 1 cc. Then each cc. will represent 0.001% Fe.

**High Iron.** If 0.02% of iron or over is present dilute 25 to 50 grams of the acid with distilled water. Add a few crystals of  $\text{KClO}_3$  and boil. Cool and add a slight excess of  $\text{NH}_4\text{OH}$ . When the iron hydroxide has settled, filter and wash with hot water. Dissolve the precipitate with  $\text{HCl}$  (1 : 1) catching the solution in a casserole. Wash the iron out of the paper. Heat the combined filtrate to boiling and titrate with standard  $\text{SnCl}_2$  solution. See page 257, Vol. I.

If antimony or arsenic are present the solution turns dark during the titration. If this occurs treat a fresh sample, diluted, with  $\text{H}_2\text{S}$  to remove As and Sb, and determine iron in the filtrate from the sulphides.

### Determination of Arsenic

**Traces of Arsenic.** Amounts less than .00005%. Take 50 grams or more of the acid and distill off the arsenic as  $\text{AsCl}_3$  according to the distillation method given on page 37. Determine arsenic in the distillate by the Gutzeit method. See page 46, Vol. I.

Amounts less than .005% may be determined directly by the Gutzeit method. When the arsenic is greater than 0.05% it may be determined by reducing the arsenic with tartaric acid and titrating with standard iodine solution, after neutralizing the acid with ammonia and adding sodium bicarbonate. 25-50 grams of the acid are taken and placed in a Kjeldahl flask and  $\frac{1}{2}$  gram of tartaric acid added together with 2 grams of fused potassium bisulphate. The acid is heated over the direct flame until the color, first becoming dark, changes to a straw color. Fuming will cause loss of arsenic and should be avoided. The acid is washed into a beaker with 250 cc. of water, then neutralized with  $\text{NH}_4\text{OH}$ , and  $\text{NaHCO}_3$  added. The titration with iodine is made in presence of starch. The end point is a blue color.

If antimony is present a separation of the arsenic must be made by distillation. 1 cc. N/10 I = .003748 g. As or .004948 g.  $\text{As}_2\text{O}_3$ .  $\text{As}_2\text{O}_3 \times 1.11616 = \text{As}_2\text{O}_5$ .

### Determination of Antimony

The arsenic is first removed by distillation as  $\text{AsCl}_3$  (page 37, Vol. I). The antimony is now distilled by adding 20 grams of zinc dissolved in 20 grams of concentrated  $\text{HCl}$ . The antimony in the distillate is determined by the modified Gutzeit method given in the chapter on Antimony, Vol. I, page 29.

### Determination of Zinc

25 to 50 cc. of the acid are evaporated to dryness in a silica dish. The residue is treated with a strong solution of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  solution. After filtering off the ferric hydroxide, the filtrate containing the zinc is neutralized with  $\text{H}_2\text{SO}_4$  and 10 cc. added in excess (sp. gr.  $\text{H}_2\text{SO}_4 = 1.84$ ). Potassium ferrocyanide is now added in such amount that the solution will contain about 2.5 per cent. Compare the turbidity with standards.

With larger amounts of zinc the zinc is determined by titrating with standard potassium ferrocyanide. See chapter on Zinc, Vol. I.

The zinc may be determined gravimetrically on a 200-gram sample. The acid is fumed off until only 2-5 cc. remains in the dish. Water is added, the solution neutralized with ammonia, sufficient dilute  $\text{H}_2\text{SO}_4$  added to make a 2.5 per cent free acid. Copper, lead, etc., are removed as sulphides by gassing with  $\text{H}_2\text{S}$ . Zinc is determined in the filtrate, after oxidation of the iron with bromine and removing it by adding  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ . Zinc is precipitated as  $\text{ZnS}$  from the filtrate made acid (2% free acid) with formic acid, by  $\text{H}_2\text{S}$ . The washed sulphide is ignited and weighed as  $\text{ZnO}$ .  $\text{ZnO} \times .8034 = \text{Zn}$ .

**Copper.** This is determined colorimetrically. 25-50 cc. of the acid are evaporated to dryness, the residue taken up with 100 cc. of water 2 cc.  $\text{HCl}$  (sp.gr. 1.19) added and copper precipitated with  $\text{H}_2\text{S}$ . The washed precipitate is dissolved in  $\text{HNO}_3$  and the solution made ammoniacal with ammonia. The color is now matched with standards containing known amounts of copper.

### Determination of Selenium

**Traces.** 10 cc. of the acid diluted with an equal volume of water are placed in a test tube and 4 or 5 drops of 1%  $\text{KI}$  solution added. Heat to boiling to expel free iodine. The brick red color is compared with standards containing known amounts of selenium made up in the same way as the sample. If sufficient selenium is present this is thrown down as a brick red finely divided precipitate.

**Standard selenium solution** is prepared by dissolving .1 g. pure  $\text{Se}$  in 5 cc.  $\text{HNO}_3$  and 10 cc.  $\text{HCl}$ . The solution is evaporated to dryness, then taken up with water and a little dilute  $\text{H}_2\text{SO}_4$  and made up to 1000 cc. 1 cc. = .0001 g.  $\text{Se}$ .

**Larger Amounts.** 500 grams of the acid is diluted by pouring into a liter of water, 100 cc. strong  $\text{HCl}$  added and the solution saturated with  $\text{SO}_2$ . The selenium is allowed to settle 15 to 20 hours, then filtered through a fine fibre filter. The precipitate is dissolved by placing the filter and precipitate in sulphuric acid nitric acid mixture 5 cc.  $\text{H}_2\text{SO}_4 + 50$  cc.  $\text{HNO}_3$ . The solution is evaporated to fumes, adding more  $\text{HNO}_3$  if the solution is dark, and again evaporated to expel  $\text{HNO}_3$ . After diluting with water and filtering, the filtrate is made up to about 100 cc. and gassed boiling hot with  $\text{H}_2\text{S}$ . The precipitated selenium is settled, filtered into a Gooch, washed with water, then alcohol and ether and dried with a current of warm air to constant weight.

**Sulphur Dioxide Determination in Sulphuric Acid.** 1-10 cc. of N/10 iodine solution are run into 200 cc. of water, starch solution is added and the acid to be tested is allowed to flow from a burette into this reagent, until the blue color disappears.

1 cc. N/10 iodine = .0032 g.  $\text{SO}_2$ .

## SULPHURIC ACID

**Hydrochloric Acid Determination in Sulphuric Acid.** 50 to 100 cc. of the acid is diluted to about 200 cc. by running the acid into chlorine-free water. 10 cc. of 1% silver nitrate solution is added and the turbidity compared against a standard made by adding standard sodium chloride solution from a burette into a solution containing an equal amount of sulphuric acid (free from chloride) diluted with water and containing silver nitrate as in case of the sample. When the turbidity is the same as the sample the number of cc. of NaCl solution are noted. The turbidity is best seen by placing the two solutions side by side on a black paper. Standard chloride solution contains .16 g. NaCl per liter. 1 cc. = .0001 g. HCl.

If considerable hydrochloric acid is present it may be determined by Volhard's method given on page 149, Vol. I. The sample of acid is diluted to about 20% strength. A measured excess of N/10  $\text{AgNO}_3$  added and the excess titrated with N/10  $\text{NH}_4\text{CNS}$  solution in presence of ferric ammonium alum.

1 cc. N/10  $\text{AgNO}_3$  = .003647 g. HCl.

## Determination of Nitric Acid

**Traces.** In absence of selenium traces of  $\text{HNO}_3$  may be determined colorimetrically. To 100 cc. of the acid  $\frac{1}{2}$  cc. saturated solution of  $\text{FeSO}_4$  is added. Comparison is made in a Nessler tube with a standard by adding to 100 cc.  $\text{H}_2\text{SO}_4$ ,  $\frac{1}{2}$  cc.  $\text{FeSO}_4$  solution and running in standard  $\text{HNO}_3$  until the color matches, the solution being stirred with a plunger during the addition. Standard  $\text{HNO}_3$  solution should contain .0001 g.  $\text{HNO}_3$  per cc.

**Larger Amounts.** See method on page 1024.

**Determination of Fluorine.** This is determined by the etch test described in Vol. I, page 224. The acid should not contain over 10%  $\text{H}_2\text{O}$ . Strengthen with oleum if necessary.

## THE ANALYSES OF OLEUM OR FUMING SULPHURIC ACID AND OF MIXED ACID

The analyses of fuming sulphuric acid and mixed acid are placed under one general scheme as the procedure for oleum is included in that of mixed acid. The term oleum is given to strong sulphuric acid containing free  $\text{SO}_3$ , the combined

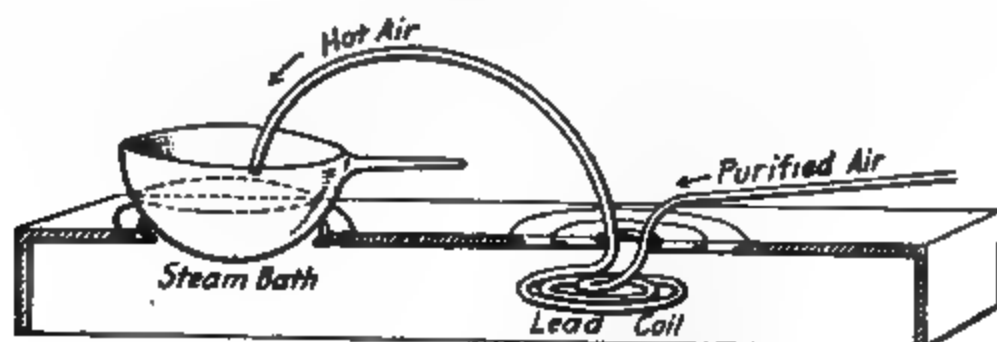


FIG. 84.—Method for Rapid Evaporation of Liquids.

water in the product decreasing (along with sulphuric acid) with the increase of free  $\text{SO}_3$  or sulphuric anhydride. Mixed acid is the technical name for the mixture of strong sulphuric acid and nitric acid or of oleum and nitric anhydride, the product being commonly used in nitrating glycerine, cotton and other materials. The analysis includes the determinations of  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{N}_2\text{O}_4$ , and in the case of oleum, the determination of  $\text{SO}_3$ . In the presence of the latter,  $\text{HNO}_3$  is assumed to lose its combined water according to the reaction:



In absence of nitric acid  $\text{SO}_3$  may be present. It is assumed that if  $\text{HNO}_3$  is present the  $\text{SO}_3$  is oxidized to  $\text{SO}_2$  with formation of  $\text{H}_2\text{SO}_4$  and the anhydrides  $\text{SO}_3$  and  $\text{N}_2\text{O}_5$  according to the reaction.



Some chemists prefer to express the reaction:



The analysis is carried out by three titrations—(a) determination of total acidity, (b) determination of sulphuric acid including  $\text{SO}_3$  free in case of oleum, (c) determination of lower oxides.

For economy of time the following order should be observed: The sample for the determination of sulphuric acid and free  $\text{SO}_3$  (oleum) should be weighed, diluted with water according to the detailed procedure and placed on the steam bath for evaporation. During the evaporation the titration for total acidity of the sample and the titration for the lower oxides are made and finally that of oleum on the evaporated sample.

### Special Reagents.

**Normal Sodium Hydroxide.** One cc. = 0.04904 gram  $\text{H}_2\text{SO}_4$ .

**Tenth Normal Potassium Permanganate.** 3.16 grams  $\text{KMnO}_4$  per liter. Standardized against N/10 solution of Sorensen's Sodium Oxalate. (See Preparation of Standard Reagents.) One cc. = 0.0019 gram  $\text{N}_2\text{O}_5$ , or 0.002351 gram  $\text{HNO}_3$ .

### Procedure. Total Acids

The sample is accurately weighed by one of the procedures recommended for strong acids. The Dely or Blay-Burkhard tubes are best for this purpose. Such a weight being taken as will require a titration between 75 and 100 cc., e.g., containing an equivalent of 3.675 grams to 4.9 grams  $\text{H}_2\text{SO}_4$ . The acid is now run under cold  $\text{CO}_2$  free water according to directions on pages 1011 and 1012, and the acid titrated with N/1 solution of  $\text{NaOH}$ .

One cc.  $\text{NaOH}$  = 0.04904 g.  $\text{H}_2\text{SO}_4$ . Calculate to per cent  $\frac{\text{cc. NaOH} \times .04904 \times 100}{\text{Weight of Acid Taken}}$ .

### Lower Oxides

Ten cc. of the sample, weighed in a pipette with capillary delivery tip, are cautiously run into about 400 cc. of cold water, keeping the delivery tip well under the water and in rapid motion to prevent overheating through local action. The mixture is titrated with N/10  $\text{KMnO}_4$  until a pink tint is obtained that does not fade in three minutes.

1 cc. N/10  $\text{KMnO}_4$  = 0.0019 g.  $\text{N}_2\text{O}_5$ . ( $\text{N}_2\text{O}_5$  to  $\text{N}_2\text{O}_4$  factor = 2.42.)

1 cc. N/10  $\text{KMnO}_4$  = 0.0046 g.  $\text{N}_2\text{O}_4$ .

1 cc. N/10  $\text{KMnO}_4$  = 0.00235 g.  $\text{HNO}_3$ . Equivalent  $\text{H}_2\text{SO}_4$  = 0.0049043 g. per cc.

1 cc. N/10  $\text{KMnO}_4$  = 0.0032035 g.  $\text{SO}_3$ .

1 cc. N/10  $\text{KMnO}_4$  = 0.0041043 g.  $\text{H}_2\text{SO}_4$ .

NOTE. With exactly N/10  $\text{KMnO}_4$  on a 10-gram sample 1 cc. = 0.01%  $\text{N}_2\text{O}_5$ .

### Sulphuric Acid and Free $\text{SO}_3$

The sample is weighed in a Dely tube and run under cold water, as in case of total acids, using in this case about 45 to 50 cc. of water in a 4-in. casserole. The solution is evaporated on the steam bath to expel the volatile acids, lower oxides and nitric. The evaporation is hastened by blowing a current of hot, dry, pure air over the sample, see Fig. 84. Instead of a casserole, a shallow glass cell, 3 inches in diameter and 1½ inches deep may be used. The air current in

this case is unnecessary. About 5 cc. of water are added and this again evaporated off. The acid thus obtained is  $\text{H}_2\text{SO}_4 + \text{SO}_3$ .

The acid is taken up with water and titrated with standard caustic, using  $\text{CO}_2$  free water and phenolphthalein indicator.

One cc. N/1 NaOH = 0.004904 gram  $\text{H}_2\text{SO}_4$ .

### Nitric Acid

This may be obtained from the above determinations according to calculations following. It may be obtained by direct titration with standard ferrous sulphate, by running a weighed amount of mixed acid into 100 cc. of cold sulphuric acid and titrating to a yellowish red tint. For the detailed procedure see Nitric Acid, page 515.

#### Calculation of Results.

##### A. Nitric Acid and $\text{SO}_3$ being Absent.

The total acidity is calculated to  $\text{SO}_3$ . Reference is made to the table for Oleum from which the per cent  $\text{H}_2\text{SO}_4$  and free  $\text{SO}_3$  are obtained.

**Example.** Suppose the total acidity in terms of  $\text{SO}_3$  was found to be 84.2. The acid contains 86%  $\text{H}_2\text{SO}_4$  and 14% free  $\text{SO}_3$ .

##### B. Nitric Acid Absent, $\text{SO}_2$ is Present in the Mixture.

**Total  $\text{SO}_3$ .** From total acidity as  $\text{SO}_3$  subtract  $\text{SO}_2 \times 1.25$  (i.e., equivalent  $\text{SO}_3$ ).

**Combined water.**  $100 - (\text{total } \text{SO}_3 + \text{SO}_2) = \text{H}_2\text{O}$ .

**Combined  $\text{SO}_3$ .**  $\text{H}_2\text{O} \times 4.4445 = \text{SO}_3$  equivalent or combined  $\text{SO}_3$ .

**Free  $\text{SO}_3$ .** Total  $\text{SO}_3 - \text{combined } \text{SO}_3 = \text{free } \text{SO}_3$ .

**Sulphuric acid.** Combined  $\text{SO}_3 + \text{H}_2\text{O}$ .

**Example.** If  $\text{SO}_2$  was found to be 2% and the total acidity in terms of  $\text{SO}_3 = 83.5\%$

Total  $\text{SO}_3 = 83.5 - (2 \times 1.25) = 81\%$ .

Water =  $100 - (81 + 2) = 17\%$ .

*Report*

Combined  $\text{SO}_3 = 17 \times 4.4445 = 75.56\%$ .

Sulphuric acid = 92.56%.

Free  $\text{SO}_3 = 81 - 75.56 = 5.44\%$ .

Free  $\text{SO}_2 = 5.44$ .

Sulphuric acid =  $75.56 + 17 = 92.56\%$ .

$\text{SO}_2 = 2.00$ . Total 100.

##### C. Nitric Acid Present and $\text{SO}_2$ Absent.

Nitric acid in presence of free  $\text{SO}_3$  is assumed to be the anhydride  $\text{N}_2\text{O}_5$ .

**$\text{N}_2\text{O}_5$ .** From the total acidity is subtracted the acidity after evaporation, both being calculated to equivalent  $\text{SO}_3$ . The difference multiplied by 1.349 = per cent  $\text{N}_2\text{O}_5$ .

**$\text{H}_2\text{O}$ .** Total  $\text{SO}_3$  (after evaporation) +  $\text{N}_2\text{O}_5$  subtracted from 100 =  $\text{H}_2\text{O}$ .

**Combined  $\text{SO}_3$ .**  $\text{H}_2\text{O} \times 4.4445 = \text{SO}_3$  equivalent to  $\text{H}_2\text{O}$ .

**Free  $\text{SO}_3$ .** Combined  $\text{SO}_3$  subtracted from total  $\text{SO}_3 = \text{free } \text{SO}_3$ .

**Sulphuric acid.** Combined  $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ .

**Example.** If total acidity = 84% in terms of  $\text{SO}_3$  and the total  $\text{SO}_3$  (after evaporation) = 82%, then the difference  $2 \times 1.349 = 2.698\%$   $\text{N}_2\text{O}_5$ .



$$\text{Water} = 100 - (82 + 2.698) = 15.302\%$$

$$\text{Combined SO}_3 = 15.302 \times 4.4445 = 68.01\%$$

$$\text{Free SO}_3 = 82 - 68.01 = 13.99\%$$

$$\text{H}_2\text{SO}_4 = 68.01 + 15.302 = 83.312\%$$

**Report**

$$\text{H}_2\text{SO}_4 = 83.312\%$$

$$\text{Free SO}_3 = 13.980\%$$

$$\text{N}_2\text{O}_5 = 2.698\%$$

Total 100.

**D.  $\text{N}_2\text{O}_5$  Required to be Reported as  $\text{HNO}_3$ , 96%.<sup>1</sup>**

$$\text{HNO}_3, 96\% = \text{SO}_3 \text{ equivalent (acid expelled by evaporation)} \times 1.64. \quad 100$$

$$-\text{per cent HNO}_3 (96\%) = \text{Oleum. Total SO}_3 \text{ in oleum} = \frac{100 \times \text{total SO}_3}{\text{per cent oleum}}$$

Reference to the oleum table will give the per cent free  $\text{SO}_3$  in the oleum.

**Example.** Suppose total acidity in terms of  $\text{SO}_3 = 84\%$  and the  $\text{SO}_3$  after evaporation  $= 82\%$ , then  $\text{HNO}_3, 96\% = \text{the difference} = 2 \times 1.64 = 3.28\% \text{ HNO}_3 (96\%)$ .

$$\text{Oleum} = 100 - 3.28 = 96.72\%$$

$$\text{Total SO}_3 \text{ in oleum} = 100 \times 82 \text{ divided by } 96.72 = 84.78.$$

From the oleum table 84.78 gives 17.10% free  $\text{SO}_3$ .**Report**

$$\text{Nitric acid, 96\%} = 3.28\%$$

$$\text{Oleum} = 96.72\%$$

$$\text{Free SO}_3 = 17.10\%$$

$$\text{Total SO}_3 = 84.78\%$$

The nitric acid and oleum make a total of 100.

<sup>1</sup> This is the usual strength of the commercial concentrated acid.

**Formulae for Diluting or Strengthening Solutions.<sup>1</sup>**

To dilute a solution with water:

$$(a) \frac{DZ}{A} = X; \quad Y = Z - X; \quad \text{or} \quad (b) \frac{A - DX}{D} = Y.$$

To dilute a strong with a weaker liquid:

$$(a) \frac{A - DZ}{A - B} = Y; \quad X - Z = Y; \quad \text{or} \quad (b) \frac{A - DX}{D - B} = Y.$$

To strengthen a weak with a stronger liquid:

$$(a) \frac{D - AZ}{C - A} = X; \quad Y = Z - X; \quad \text{or} \quad (b) \frac{D - AY}{C - D} = X.$$

*A* = actual concentration of the solution that is to be corrected;

*B* = concentration of the diluting solution;

*C* = concentration of the strengthening solution;

*D* = desired concentration;

*X* = amount of the stronger solution to be added, taken or prepared;

*Y* = amount of weaker solution to be added or taken;

*Z* = amount of solution desired or given.

All data are in terms of weight of the constituents.

<sup>1</sup>Compiled by J. B. Barnitt.

## SULPHURIC ACID

By W. C. FERGUSON AND H. P. TALBOT

Degrees Baumé.	Specific Gravity 60° F. 60° F.	Degrees Twaddell.	Per Cent H <sub>2</sub> SO <sub>4</sub> .	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.*	Pounds O. V. in 1 Cubic Foot.
0	1.0000	0.0	0.00	62.37	0.00	0.00
1	1.0069	1.4	1.02	62.80	1.09	0.00
2	1.0140	2.8	2.08	63.24	2.23	1.41
3	1.0211	4.2	3.13	63.69	3.36	2.14
4	1.0284	5.7	4.21	64.14	4.52	2.90
5	1.0357	7.1	5.28	64.60	5.67	3.66
6	1.0432	8.6	6.37	65.06	6.84	4.45
7	1.0507	10.1	7.45	65.53	7.99	5.24
8	1.0584	11.7	8.55	66.01	9.17	6.06
9	1.0662	13.2	9.66	66.50	10.37	6.90
10	1.0741	14.8	10.77	66.99	11.56	7.74
11	1.0821	16.4	11.89	67.49	12.76	8.61
12	1.0902	18.0	13.01	68.00	13.96	9.49
13	1.0985	19.7	14.13	68.51	15.16	10.39
14	1.1069	21.4	15.25	69.04	16.36	11.30
15	1.1154	23.1	16.38	69.57	17.58	12.23
16	1.1240	24.8	17.53	70.10	18.81	13.19
17	1.1328	26.6	18.71	70.65	20.08	14.18
18	1.1417	28.3	19.89	71.21	21.34	15.20
19	1.1508	30.2	21.07	71.78	22.61	16.23
20	1.1600	32.0	22.25	72.35	23.87	17.27
21	1.1694	33.9	23.43	72.94	25.14	18.34
22	1.1789	35.8	24.61	73.53	26.41	19.42
23	1.1885	37.7	25.81	74.13	27.69	20.53
24	1.1983	39.7	27.03	74.74	29.00	21.68

Sp. Gr. determinations were made at 60° F., compared with water at 60° F.

From the Sp. Grs., the corresponding degrees Baumé were calculated by the following formula: Baumé = 145 - 145/Sp. Gr.

Baumé Hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

\* 66° Baumé = Sp. Gr. 1.8354 = Oil of Vitriol (O. V.).

1 cu. ft. water at 60° F. weighs 62.37 lbs. av.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

H<sub>2</sub>SO<sub>4</sub> = 100 per cent.

	% H <sub>2</sub> SO <sub>4</sub>	% O. V.	% 60°
O. V.	= 93.19	= 100.00	= 119.98
60°	= 77.67	= 83.35	= 100.00
50°	= 62.18	= 66.72	= 80.06

## SULPHURIC ACID (Continued)

Degrees Baumé.	° Freezing (Melting) Point.	APPROXIMATE BOILING POINTS			
		50° B.	295° F.	60° "	386° "
0	32.0	61° "	400° "	62° "	415° "
1	31.2	63° "	415° "	63° "	432° "
2	30.5	64° "	431° "	64° "	451° "
3	29.8	65° "	455° "	65° "	485° "
4	28.9	66° "	538° "		
5	28.1				
6	27.2				
7	26.3				
8	25.1				
9	24.0				
		FIXED POINTS			
10	22.8	Specific Gravity.	Per Cent H <sub>2</sub> SO <sub>4</sub> .	Specific Gravity.	Per Cent H <sub>2</sub> SO <sub>4</sub> .
11	21.5	1.0000	.00	1.5281	62.34
12	20.0	1.0048	.71	1.5440	63.79
13	18.3	1.0347	5.14	1.5748	66.51
14	16.6	1.0649	9.48	1.6272	71.00
15	14.7	1.0992	14.22	1.6679	74.46
16	12.6	1.1353	19.04	1.7044	77.54
17	10.2	1.1736	23.94	1.7258	79.40
18	7.7	1.2105	28.55	1.7472	81.32
19	4.8	1.2513	33.49	1.7700	83.47
		1.2951	38.64	1.7959	86.36
20	+ 1.6	1.3441	44.15	1.8117	88.53
21	- 1.8	1.3947	49.52	1.8194	89.75
22	- 6.0	1.4307	53.17	1.8275	91.32
23	- 11	1.4667	56.68	1.8354	93.19
24	- 16	1.4822	58.14		

Acids stronger than 66° Bé. should have their percentage compositions determined by chemical analysis.

\* Calculated from Pickering's results, Jour. of Lon. Ch. Soc., vol. 57, p. 363.

AUTHORITIES — W. C. FERGUSON; H. P. TALBOT.

This table has been approved and adopted as a standard by the Manufacturing Chemists' Association of the United States.

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*Executive Committee*

New York, June 23, 1904.

## SULPHURIC ACID (Continued)

Degrees Baumé.	Specific Gravity 60° F.	Degrees Twaddell.	Per Cent $H_2SO_4$ .	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cubic Foot.
25	1.2083	41.7	28.68	75.36	30.34	22.87
26	1.2185	43.7	29.53	76.00	31.69	24.08
27	1.2288	45.8	30.79	76.64	33.04	25.32
28	1.2393	47.9	32.05	77.30	34.39	26.58
29	1.2500	50.0	33.33	77.96	35.76	27.88
30	1.2609	52.2	34.63	78.64	37.10	29.22
31	1.2719	54.4	35.93	79.33	38.55	30.58
32	1.2832	56.7	37.20	80.03	40.00	32.00
33	1.2946	58.9	38.58	80.74	41.40	33.42
34	1.3063	61.3	39.92	81.47	42.83	34.90
35	1.3182	63.6	41.27	82.22	44.28	36.41
36	1.3303	66.1	42.63	82.97	45.74	37.95
37	1.3426	68.5	43.99	83.74	47.20	39.53
38	1.3551	71.0	45.35	84.52	48.66	41.13
39	1.3679	73.6	46.72	85.32	50.13	42.77
40	1.3810	76.2	48.10	86.13	51.61	44.45
41	1.3942	78.8	49.47	86.96	53.08	46.16
42	1.4078	81.6	50.87	87.80	54.58	47.92
43	1.4216	84.3	52.26	88.67	56.07	49.72
44	1.4356	87.1	53.66	89.54	57.58	51.56
45	1.4500	90.0	55.07	90.44	59.09	53.44
46	1.4646	92.9	56.48	91.35	60.60	55.36
47	1.4796	95.9	57.90	92.28	62.13	57.33
48	1.4948	99.0	59.32	93.23	63.65	59.34
49	1.5104	102.1	60.75	94.20	65.18	61.40
50	1.5263	105.3	62.18	95.20	66.72	63.52
51	1.5426	108.5	63.66	96.21	68.31	65.72
52	1.5591	111.8	65.13	97.24	69.89	67.96
53	1.5761	115.2	66.60	98.30	71.50	70.28
54	1.5934	118.7	68.13	99.38	73.11	72.66
55	1.6111	122.2	69.65	100.48	74.74	75.10
56	1.6292	125.8	71.17	101.61	76.37	77.60
57	1.6477	129.5	72.75	102.77	78.07	80.23
58	1.6667	133.3	74.36	103.95	79.79	82.95
59	1.6860	137.2	75.99	105.16	81.54	85.75

## SULPHURIC ACID (Continued)

Degree Baumé.	• Freezing (Melting) Point, °F.	ALLOWANCE FOR TEMPERATURE			
25	-23	At 10° B <sub>é</sub> . .029° B <sub>é</sub> . or .00023 Sp. Gr. = 1° F.			
26	-30	" 20° " .036° " .00034 " = 1° "			
27	-39	" 30° " .035° " .00039 " = 1° "			
28	-49	" 40° " .031° " .00041 " = 1° "			
29	-61	" 50° " .028° " .00045 " = 1° "			
30	-74	" 60° " .026° " .00053 " = 1° "			
31	-82	" 63° " .026° " .00057 " = 1° "			
32	-96	" 66° " .0235° " .00054 " = 1° "			
33	-97				
34	-91				
35	-81				
36	-70				
37	-60				
38	-53				
39	-47				
		Per Cent 60° Baumé.	Pounds 60° Baumé in 1 Cubic Foot.	Per Cent 50° Baumé.	Pounds 50° Baumé in 1 Cubic Foot.
40	-41	61.93	53.34	77.36	66.63
41	-35	63.69	55.39	79.56	69.19
42	-31	65.50	57.50	81.81	71.83
43	-27	67.28	59.66	84.05	74.53
44	-23	69.09	61.86	86.30	77.27
45	-20	70.90	64.12	88.56	80.10
46	-14	72.72	66.43	90.83	82.98
47	-15	74.55	68.79	93.12	85.93
48	-18	76.37	71.20	95.40	88.94
49	-22	78.22	73.68	97.70	92.03
50	-27	80.06	76.21	100.00	95.20
51	-33	81.96	78.85	102.38	98.50
52	-39	83.86	81.54	104.74	101.85
53	-49	85.79	84.33	107.15	105.33
54	-60	87.72	87.17	109.57	108.89
55	..	89.67	90.10	112.01	112.55
56	..	91.63	93.11	114.46	116.30
57	..	93.67	96.26	117.00	120.24
58	..	95.74	99.52	119.59	124.31
59	- 7	97.84	102.89	122.21	128.52

## SULPHURIC ACID (Continued)

Degrees Baumé.	Specific Gravity 60° F. 60°	Degrees Twaddell.	Per Cent $H_2SO_4$ .	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cubic Foot.
60	1.7059	141.2	77.67	106.40	83.35	88.63
61	1.7262	145.2	79.43	107.66	85.23	91.76
62	1.7470	149.4	81.30	108.91	87.24	95.06
63	1.7683	153.7	83.34	110.29	89.42	98.63
64	1.7901	158.0	85.66	111.65	91.92	102.63
64½	1.7957	159.1	86.33	112.00	92.64	103.75
64½	1.8012	160.2	87.04	112.34	93.40	104.93
64½	1.8068	161.4	87.81	112.69	94.23	106.19
65	1.8125	162.5	88.61	113.05	95.13	107.54
65½	1.8182	163.6	89.55	113.40	96.10	108.97
65½	1.8239	164.8	90.50	113.76	97.22	110.60
65½	1.8297	165.9	91.80	114.12	98.51	112.42
66	1.8354	167.1	93.19	114.47	100.00	114.47

Degrees Baumé.	Freezing (Melting) Point.	Per Cent 60° Baumé.	Pounds 60° Baumé in Cubic Foot.	Per Cent 50° Baumé.	Pounds 50° Baumé in Cubic Foot.
60	+12.6	100.00	106.40	124.91	132.91
61	27.3	102.27	110.10	127.74	137.52
62	39.1	104.67	114.05	130.75	142.47
63	46.1	107.30	118.34	134.03	147.82
64	46.4	110.29	123.14	137.76	153.81
64½	43.6	111.15	124.49	138.84	155.50
64½	41.1	112.06	125.89	139.93	157.25
64½	37.9	113.05	127.40	141.22	159.14
65	33.1	114.14	129.03	142.57	161.17
65½	24.6	115.30	130.75	144.02	163.32
65½	13.4	116.65	132.70	145.71	165.76
65½	- 1	118.19	134.88	147.63	168.44
66	-29	119.98	137.34	149.87	171.56

## XI.—SULPHURIC ACID TABLE

94-100%  $H_2SO_4$ 

By H. B. BISHOP

Bé.	Sp. Gr. at 60° F.	Per Cent. $H_2SO_4$ .	Wt. 1 Cu. Ft.	Allowance for Temperature.
66	1.8354	93.19	114.47	At 94% .00054 sp.gr. = 1° F.
66.12	1.8381	94.00	114.64	" 96 .0053 " = 1° F.
66.23	1.8407	95.00	114.80	" 97.5 .00052 " = 1° F.
66.31	1.8427	96.00	114.93	" 100 .00052 " = 1° F.
66.36	1.8437	97.00	114.99	
66.36	1.8439	97.50	114.99	
66.36	1.8437	98.00	114.99	
66.30	1.8424	99.00	114.91	
66.16	1.8391	100.00	114.70	

## FUMING SULPHURIC ACID EQUIVALENTS

Total SO <sub>3</sub>	Equivalent H <sub>2</sub> SO <sub>4</sub>	Per Cent H <sub>2</sub> SO <sub>4</sub>	Per Cent Free SO <sub>3</sub>	Total SO <sub>3</sub>	Equivalent H <sub>2</sub> SO <sub>4</sub>	Per Cent H <sub>2</sub> SO <sub>4</sub>	Per Cent Free SO <sub>3</sub>
81.63	100.00	100	0	90.82	111.25	50	50
81.82	100.23	99	1	91.00	111.48	49	51
82.00	100.46	98	2	91.18	111.70	48	52
82.18	100.67	97	3	91.37	111.93	47	53
82.37	100.90	96	4	91.55	112.15	46	54
82.55	101.13	95	5	91.73	112.37	45	55
82.73	101.35	94	6	91.92	112.60	44	56
82.92	101.58	93	7	92.10	112.82	43	57
83.10	101.80	92	8	92.29	113.05	42	58
83.29	102.03	91	9	92.47	113.28	41	59
83.47	102.25	90	10	92.65	113.50	40	60
83.65	102.47	89	11	92.84	113.73	39	61
83.84	102.70	88	12	93.02	113.95	38	62
84.02	102.92	87	13	93.20	114.17	37	63
84.20	103.15	86	14	93.39	114.40	36	64
84.39	103.38	85	15	93.57	114.62	35	65
84.57	103.60	84	16	93.76	114.85	34	66
84.75	103.82	83	17	93.94	115.08	33	67
84.94	104.05	82	18	94.12	115.30	32	68
85.12	104.27	81	19	94.31	115.53	31	69
85.31	104.50	80	20	94.49	115.75	30	70
85.49	104.73	79	21	94.67	115.97	29	71
85.67	104.95	78	22	94.86	116.20	28	72
85.86	105.18	77	23	95.04	116.42	27	73
86.04	105.40	76	24	95.22	116.65	26	74
86.22	105.63	75	25	95.41	116.88	25	75
86.41	105.85	74	26	95.59	117.10	24	76
86.59	106.07	73	27	95.78	117.33	23	77
86.78	106.30	72	28	95.96	117.55	22	78
86.96	106.53	71	29	96.14	117.77	21	79
87.14	106.75	70	30	96.33	118.00	20	80
87.33	106.98	69	31	96.51	118.22	19	81
87.51	107.20	68	32	96.69	118.45	18	82
87.69	107.42	67	33	96.88	118.68	17	83
87.88	107.65	66	34	97.06	118.90	16	84
88.06	107.87	65	35	97.25	119.13	15	85
88.24	108.10	64	36	97.43	119.35	14	86
88.43	108.33	63	37	97.61	119.57	13	87
88.61	108.55	62	38	97.80	119.80	12	88
88.80	108.78	61	39	97.98	120.03	11	89
88.98	109.00	60	40	98.16	120.25	10	90
89.16	109.22	59	41	98.35	120.48	9	91
89.35	109.45	58	42	98.53	120.70	8	92
89.53	109.67	57	43	98.71	120.92	7	93
89.71	109.90	56	44	98.90	121.15	6	94
89.90	110.13	55	45	99.08	121.37	5	95
90.08	110.35	54	46	99.27	121.60	4	96
90.27	110.58	53	47	99.45	121.83	3	97
90.45	110.80	52	48	99.63	122.05	2	98
90.63	111.02	51	49	99.82	122.28	1	99
				100.00	122.50	0	100

Compiled from the table by H. B. Bishop, Van Nostrand's Chemical Annual, 1913.



## METHOD OF ANALYSIS OF CHLOROSULPHONIC ACID

Chlorosulphonic acid,  $\text{SO}_3 \cdot \text{HCl}$ , decomposes to  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  on addition of water, the reaction being violent. Considerable care must be exercised to prevent loss of acid during dilution with water for examination of the product. The following method of analysis has been found satisfactory:

**Total Acidity.** Three to four grams of the chlorosulphonic acid are weighed in a D li tube or small glass bulb. About 25 cc. of distilled (neutral) water and about 10 cc. less  $\text{NaOH}$  (normal strength) than is necessary to neutralize the sample (i.e.,  $\frac{\text{weight sample}}{0.04001} - 10 = \text{cc. NaOH to be taken}$ ) are placed in a heavy

wall glass bottle (250-300 cc. capacity). If the sample is weighed in a D li tube it is run into the  $\text{NaOH}$  solution according to the procedure described on page 506. If the bulb is used, the bottle, with the sample inserted, is stoppered, wrapped in a towel and shaken vigorously until the bulb breaks and the acid mixes with the water and  $\text{NaOH}$ . The excess of acid is now titrated with  $\text{N. NaOH}$ , using phenolphthalein or methyl red indicator. The total acidity is calculated to  $\text{SO}_3$  and recorded as per cent  $\text{SO}_3$ .

**Titration of Chloride.** The  $\text{NaCl}$  formed is titrated with  $\text{N}/3 \text{ AgNO}_3$  solution, using  $\text{K}_2\text{CrO}_4$  indicator. The cc. of the reagent are calculated to the equivalent  $\text{HCl}$ . Since  $\text{NaOH}$  is apt to contain  $\text{NaCl}$ , the blank is subtracted to obtain the true  $\text{HCl}$  equivalent in the sample. The per cent  $\text{HCl}$  is calculated.

The Composition of the Acid is now determined as follows:

- Total acid as per cent  $\text{SO}_3 = a$ .
- $\text{HCl}$  obtained by titration of the neutralized solution (made faintly acid) with  $\text{N}/3 \text{ AgNO}_3$  (the  $\text{HCl}$  blank for the  $\text{NaOH}$  used in (a) having been subtracted)  $= b$ . The  $\text{HCl}$  is converted to its equivalent  $\text{SO}_3$  by multiplying by  $1.0978 = b'$ .
- $\text{SO}_3$  (combined and free). The  $\text{SO}_3$  equivalent of  $\text{HCl}$  obtained in b is subtracted from the total acidity as  $\text{SO}_3$  of (a) is  $a - b' = \text{SO}_3 \text{ total}$ .
- $100 - (\text{per cent } \text{SO}_3 + \text{per cent } \text{HCl}) = \text{per cent } \text{H}_2\text{O}$  in sample. This is combined with a portion of the  $\text{SO}_3$  as  $\text{H}_2\text{SO}_4$ . Calculate to per cent  $\text{H}_2\text{SO}_4$  by multiplying by 5.4444. Allowance must be made for impurities if present.<sup>1</sup>
- The  $\text{SO}_3$  combined with  $\text{H}_2\text{O}$  is subtracted from the total  $\text{SO}_3$  of (c). The result is the  $\text{SO}_3$  of the chlorosulphonic acid and free  $\text{SO}_3$  (if any).

By inspection it is possible to ascertain whether the product contains free  $\text{SO}_3$  or free  $\text{HCl}$  since  $\text{SO}_3 \cdot \text{HCl}$  are in the proportion 31.29 per cent  $\text{HCl}$  and 68.71 per cent  $\text{SO}_3$ , i.e.,  $\text{HCl} : \text{SO}_3 :: 1 : 2.2$ .

If  $\text{SO}_3$  is in excess. The  $\text{HCl}$  is calculated to  $\text{SO}_3 \cdot \text{HCl}$  by multiplying by 3.1956, the result is the per cent chlorosulphonic acid in the sample.

Free  $\text{SO}_3$  is obtained by subtracting per cent  $\text{SO}_3 \cdot \text{HCl} + \text{per cent } \text{H}_2\text{SO}_4$  from 100.

If  $\text{HCl}$  is in excess. The per cent  $\text{SO}_3$  obtained in (e) is multiplied by 1.4555; the result is the per cent chlorosulphonic acid.

Free  $\text{HCl}$  is obtained by subtracting per cent  $\text{SO}_3 \cdot \text{HCl} + \text{per cent } \text{H}_2\text{SO}_4$  from 100.

Results are reported as per cent  $\text{SO}_3 \cdot \text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , free  $\text{SO}_3$  or free  $\text{HCl}$ .

Factors:

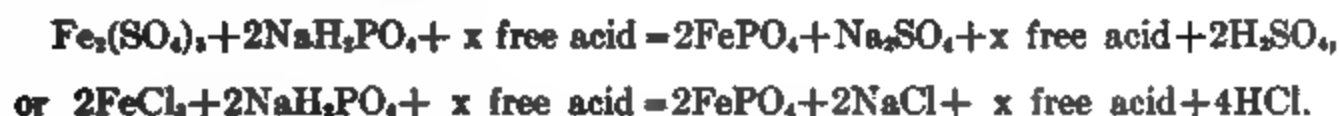
$\text{HCl} \times 1.0978 = \text{SO}_3$ ,  $\text{HCl} \times 3.1956 = \text{SO}_3 \cdot \text{HCl}$  and  $\text{HCl} \times 2.1959 = \text{SO}_3$  in  $\text{SO}_3 \cdot \text{HCl}$ .  
 $\text{SO}_3 \times 0.8998 = \text{HCl}$ ,  $\text{SO}_3 \times 1.4555 = \text{SO}_3 \cdot \text{HCl}$  and  $\text{SO}_3 \times 0.4554 = \text{HCl}$  in  $\text{SO}_3 \cdot \text{HCl}$ .  
 $\text{H}_2\text{O} \times 5.4444 = \text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4 \times 0.1837 = \text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4 \times 0.7436 = \text{HCl}$ .  
 $\text{NaCl} \times 0.6238 = \text{HCl}$ ,  $\text{SO}_3 \cdot \text{HCl} = 31.29 \text{ per cent HCl and } 68.71 \text{ per cent SO}_3$ .

<sup>1</sup>  $(100 - \text{impurities non-titratable}) - (\% \text{SO}_3 + \% \text{HCl}) = \% \text{H}_2\text{O}$ .

## VOLUMETRIC ESTIMATION OF FREE ACID IN PRESENCE OF IRON SALTS

The red precipitate formed when solutions containing iron are titrated with caustic makes it difficult to detect the end-point of neutralization; the method suggested by C. A. Ahlum<sup>1</sup> takes advantage of the white compound formed by precipitating the iron as a phosphate and the fact that monosodium phosphate is neutral to methyl-orange indicator.

### Reactions



The acid equivalent to ferric iron is deducted from the total acid found, the excess acid being due to the free acid in the solution.

**Procedure.** To the solution containing the iron and free acid is added an excess of C.P. solution of monosodium phosphate (neutral to methyl-orange), and then a few drops of the indicator. The acidity of the solution is now determined by titration with standard caustic in the usual way, the solution being cold. From this titration the total free and combined acid are calculated.

Iron is now determined in a separate portion by titration with stannous chloride or dichromate.

### Calculation.

(A)  $\text{Fe}_2\text{O}_3 \times 1.2285 = \text{g. H}_2\text{SO}_4 \text{ (combined)}$ .  $\text{Fe}_2\text{O}_3 \times 0.9135 = \text{g. HCl (combined)}$ .

(B) One cc. N/5 NaOH = .00981 gram  $\text{H}_2\text{SO}_4$  or .00729 gram HCl.

Total acid (B) minus combined acid (A) = *free acid*.

<sup>1</sup> C. A. Ahlum, *The Analyst*, **31**, 168, 1906.

## ORGANIC ACIDS

Titration of organic acids are made preferably with phenolphthalein. Methyl orange cannot be used. The water used for diluting the organic acid must be free of carbon dioxide.

### ANALYSIS OF FORMIC ACID

Formic acid occurs in solutions of varying strength, i.e., 30, 50, 75, 90%, etc. The impurities that are frequently present are sulphuric and hydrochloric acid. If formic acid alone is present it may be determined by direct titration. 1 cc. N/10 NaOH = 0.004602 gram formic acid. In presence of other acids the following method is recommended.

**Procedure.** About 10 grams of the sample weighed in a tared bottle (Blay-Burkhard form is convenient) is run into about 200 cc. of distilled water in a graduated flask of 500 cc. capacity and made to volume. 50 cc. of this diluted sample pipetted into an Erlenmeyer flask is made alkaline with  $\text{Na}_2\text{CO}_3$  solution. After warming a measured excess of N/10  $\text{KMnO}_4$  is added. Formic acid is oxidized to  $\text{H}_2\text{O} + \text{CO}_2$  and a precipitate of  $\text{MnO}_2$  is thrown down. 10 cc. of dilute  $\text{H}_2\text{SO}_4$  are added and a measured volume of N/10 oxalic acid is added until all of the precipitate has dissolved and the permanganate color has disappeared. The excess of oxalic acid is now titrated with N/10 permanganate reagent. From this the cc.  $\text{KMnO}_4$  required by the formic acid is obtained.

$$1 \text{ cc. N/10 KMnO}_4 = 0.002301 \text{ gram formic acid}$$

The equivalent cc. values of the  $\text{KMnO}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$  should be obtained by titration.

**Sulphuric Acid.** This is conveniently determined on about 20 gram sample diluted to 200 cc. by precipitation with  $\text{BaCl}_2$  according to the standard procedure.

$$\text{BaSO}_4 \times 0.4202 = \text{H}_2\text{SO}_4$$

**Hydrochloric Acid.** This may be determined on a 20 gram sample by precipitation with  $\text{AgNO}_3$  in presence of 5 cc. conc.  $\text{HNO}_3$ , the sample having been diluted to about 200 cc.

$$\text{AgCl} \times 0.2545 = \text{HCl}$$

## ANALYSIS OF ACETIC ANHYDRIDE—ACIDITY METHOD

Acetic anhydride  $\begin{matrix} \text{CH}_3\text{CO} \\ \text{CH}_3\text{CO} \end{matrix} \text{O}$  is a volatile, colorless liquid, possessing a characteristic sharp penetrating odor. The vapor is very irritating to the nose and eyes. The pure anhydride boils at  $137^\circ \text{C}$ . Mixed with water strong acetic anhydride settles out into a distinct layer very similar to carbon disulphide. It hydrolyzes slowly forming a solution of acetic acid. When below 50% in strength (the diluting liquid being acetic acid) the product mixes readily with water at ordinary temperatures ( $20^\circ \text{C}$ .). Distinct separation from water takes place when the strength of the anhydride is over 55%, the product being added to the water dropwise. The separation becomes more decided with increase of the percentage of anhydride.

The analysis consists in titrating the acetic acid formed by the hydrolysis of the anhydride. Since the product is volatile it is weighed in stoppered bottles. Low results are obtained if sufficient time is not allowed for complete hydrolysis.

**Procedure.** A sample of approximately 5 to 5.5 grams is weighed in a bottle 6 to 8 cc. in capacity. A small 2-dram apothecaries' bottle with No. 00 rubber stopper is satisfactory. The stopper is fitted loosely and the bottle containing the sample is immersed in 100 cc. of normal NaOH and 300 cc. of distilled water in a 500 cc. "salt mouth" bottle with rubber stopper. The bottle is closed tightly and shaken to free the small rubber stopper from the weighing bottle, and permit the sample to mix with the reagent. After hydrolyzing for at least one hour the sample is titrated with N/5  $\text{H}_2\text{SO}_4$  to determine the excess of N/1 NaOH, using phenolphthalein indicator.

**Calculation.**

$$\frac{\text{cc. NaOH} \times 0.06003}{\text{wt. sample}} \times 100 = \% \text{CH}_3\text{COOH}$$

$$(\% \text{CH}_3\text{COOH} - 100) \times 5.665 = \% (\text{CH}_3\text{CO})_2\text{O}.$$

**Example.** If the sample titrated 101%  $\text{CH}_3\text{COOH}$  then

$$(101 - 100) \times 5.665 = 5.665\% (\text{CH}_3\text{CO})_2\text{O}.$$

**Notes.** 100 per cent.  $(\text{CH}_3\text{CO})_2\text{O} = 117.65\% \text{CH}_3\text{COOH}$ .

$$\begin{aligned} \text{Per cent. Anhydride} &= \frac{A - 100}{117.65 - 100} \times 100 \\ &= (A - 100)5.665. \end{aligned}$$

$$A = \% \text{CH}_3\text{COOH by titration.}$$

$$\text{H}_2\text{SO}_4 \times 1.2241 = \text{CH}_3\text{COOH}.$$

### DETERMINATION OF ACETIC ANHYDRIDE— ANILINE METHOD

**Procedure.** The analysis should be carried out in duplicate runs, each portion being determined as follows: Two cc. of anhydride are run from a burette into a tared 5 cc. weighing bottle and carefully weighed, the bottle being stoppered. The sample is now placed in an Erlenmeyer flask containing 50 cc. N NaOH and 50 cc. distilled water, the stopper of the bottle being loosened so that the anhydride mixes with the alkali. After forty minutes with occasional shaking of the flask to assist the mixing, the residual NaOH is titrated with N  $\text{H}_2\text{SO}_4$ , in presence of phenolphthalein indicator, 2 or 3 cc. of acid added in excess. After standing fifteen minutes longer the excess acid is titrated back with N/10 NaOH. From the amount of N NaOH required by the anhydride calculate the amount of N NaOH required by 100 grams of the sample. Record this as "A."

Twenty cc. of recently redistilled, perfectly dry aniline are run into a 50 cc. tared weighing bottle and 2 cc. of the anhydride added from a burette. The sample is added slowly, swirling the aniline to get an equal distribution. When the mixture has cooled to room temperature the weight of the anhydride is determined (the aniline and bottle having previously been weighed). After an hour the mixture is transferred to a 500 cc. volumetric flask and the solution diluted to mark with neutral alcohol and distilled water (1 : 1). Fifty cc. of this solution are titrated with N/10 NaOH. From the number of cc. required calculate the cc. N NaOH corresponding to the residual acetic acid from 100 grams of the sample. Record this as "B."

Then A-B corresponds to one half the anhydride in 100 grams of the sample. This value multiplied by 0.10207 = per cent acetic anhydride.

0.10207 = molecular weight of acetic anhydride divided by 1000

**Correction for Mineral Acids if Present.** In weighed portions (10 grams) determine hydrochloric acid by precipitation with  $\text{AgNO}_3$  and sulphuric acid by precipitation with  $\text{BaCl}_2$  in the usual way, the samples having hydrolyzed in 100 cc. portions of water. From the percentages of mineral acids present calculate to cc. normal equivalents and deduct from the titrations above, or calculate the anhydride equivalent and make deduction.

$$\begin{aligned} 1 \text{ cc. N H}_2\text{SO}_4 &= .04904 \text{ g. } 1 \text{ cc. N HCl} = .03647 \text{ g. } 1 \text{ cc. N CH}_3\text{COOH} \\ &= .06003 \text{ g. CH}_3\text{COOH} \times 0.85 = (\text{CH}_3\text{CO})_2\text{O} \\ \text{H}_2\text{SO}_4 \times 1.0404 &= (\text{CH}_3\text{CO})_2\text{O}, \quad \text{HCl} \times 1.3889 = (\text{CH}_3\text{CO})_2\text{O} \end{aligned}$$

## ANALYSIS OF ACETIC ACID

The acidity of acetic acid may be determined by titration with standard caustic, using phenolphthalein as indicator.

About 4 to 5 grams of glacial acetic acid or a corresponding amount of dilute acid are taken for analysis, being weighed out in a weighing bottle or other suitable container used for strong and weak acids. The acid is mixed with about 250 cc. of water and titrated in the presence of phenolphthalein indicator with normal caustic.

One cc. N/1 NaOH = 0.06003 gram  $\text{CH}_3\text{COOH}$ .

### Impurities in Acetic Acid

The more important impurities that are looked for in commercial acetic acid are formic acid, furfural, acetone, sulphuric acid, sulphurous acid, hydrochloric acid, metals.

In the examination of the acid the physical appearance—turbidity and color are noted.

### Formic Acid in Acetic

**Qualitative.** Ten cc. of the acid (glacial diluted 1 : 10) are heated with 1 gram of sodium acetate and 5 cc. of 5 per cent mercuric chloride solution. A turbidity indicates formic acid.

**Quantitative.** Five grams of glacial acetic acid or corresponding quantity of dilute acid are treated with 5 grams of sodium acetate and 40 cc. of mercuric chloride solution (5 per cent) and 30 cc. of water added. The mixture is heated for two hours in a flask with a return condenser, the flask being surrounded by steam. The precipitated mercurous chloride,  $\text{Hg}_2\text{Cl}_2$ , is filtered off, dried and weighed.

Weight of  $\text{Hg}_2\text{Cl}_2 \times 0.0977$  = formic acid equivalent.

### Furfural in Acetic Acid

**Qualitative.** Aniline dissolved in pure glacial acetic acid (5 cc. aniline in 2 cc. glacial acetic acid) and added to 100 cc. of the sample will produce a red color in presence of furfural.

**Quantitative.** The test may be made quantitative by comparing the color produced with standard solutions containing known amounts of furfural. One gram of redistilled furfural is dissolved in 100 cc. of 95 per cent alcohol. 1 cc. of this solution is diluted to 100 cc. with 95 per cent alcohol. 1 cc. = 0.0001 gram of the reagent.

**Test for furfural in vinegar.** Fifty cc. of the vinegar is neutralized with sodium hydroxide, and 15 to 20 cc. are distilled. Two cc. of colorless aniline and 15 cc. of hydrochloric acid (1:12) added. The mixture is warmed to about 15° C. for a few minutes and the color compared with standards prepared in the same way.

### Gravimetric Method with Phloroglucid

Place a quantity of the material, chosen so that the weight of phloroglucid obtained shall not exceed 0.300 gram, in a flask, together with 100 cc. of 12 per cent hydrochloric acid (specific gravity, 1.06), and several pieces of recently heated pumice stone. Place the flask on a wire gauze, connect with a condenser, and heat, rather gently at first, and so regulate as to distill over 30 cc. in about ten minutes, the distillate passing through a small filter paper. Replace the 30 cc. driven over by a like quantity of the dilute acid added by means of a separatory funnel in such a manner as to wash down the particles adhering to the sides of the flask, and continue the process until the distillate amounts to 360 cc. To the completed distillate gradually add a quantity of phloroglucid (purified if necessary) dissolved in 12 per cent hydrochloric acid and thoroughly stir the resulting mixture. The amount of phloroglucid used should be about double that of the furfural expected. The solution first turns yellow, then green, and very soon an amorphous greenish precipitate appears, which grows rapidly darker, till it finally becomes almost black. Make the solution up to 400 cc. with 12 per cent hydrochloric acid, and allow to stand overnight.

Filter the amorphous black precipitate into a tared Gooch crucible through an asbestos felt, wash carefully with 150 cc. of water in such a way that the water is not entirely removed from the crucible until the very last, then dry for four hours at the temperature of boiling water, cool and weigh, in a weighing bottle, the increase in weight being reckoned as phloroglucid. To calculate the furfural, pentose, or pentosan from the phloroglucid, use the following formulas given by Kröber:

(a) For weight of phloroglucid "a" under 0.03 gram.

$$\text{Furfural} = (a + 0.0052) \times 0.5170.$$

$$\text{Pentoses} = (a + 0.0052) \times 1.0170.$$

$$\text{Pentosans} = (a + 0.0052) \times 0.8949.$$

(b) For weight of phloroglucid "a" over 0.300 gram.

$$\text{Furfural} = (a + 0.0052) \times 0.5180.$$

$$\text{Pentoses} = (a + 0.0052) \times 1.0026.$$

$$\text{Pentosans} = (a + 0.0052) \times 0.8824.$$

For weight of phloroglucid "a" from 0.03 to 0.300 gram use Kröber's table or the following formulas:

$$\text{Furfural} = (a + 0.0052) \times 0.5185.$$

$$\text{Pentoses} = (a + 0.0052) \times 1.0075.$$

$$\text{Pentosans} = (a + 0.0052) \times 0.8866.$$

The phloroglucid is purified by recrystallization from hydrochloric acid. For details of the procedure see Bulletin 107, U. S. Dept. of Agriculture, Bureau of Chemistry. (1912, page 54.)

### Acetone in Acetic Acid

Fifteen grams of glacial acetic acid, or a corresponding amount of weak acid, is treated with 70 cc. potassium hydroxide (10 per cent solution), or sufficient caustic

to make the solution slightly alkaline. The solution is cooled and 25 cc. N/5 iodine solution added and sufficient hydrochloric acid to make the mixture faintly acid. The excess of iodine is titrated with N/5 sodium thiosulphate, using starch indicator. The total iodine solution taken minus the equivalent cc. of thiosulphate = the iodine combined with the acetone, then the weight of iodine in grams multiplied by 0.07612 = grams acetone in the sample.

### Sulphuric Acid in Acetic Acid

This is best determined by the turbidity test. About 5 cc. of the sample are taken and 1 drop of hydrochloric acid and half a cc. of 10 per cent barium chloride. The turbidity is now compared with a standard pure acetic acid solution containing a known quantity of  $\text{BaSO}_4$ , the standard being added to a comparison cylinder until the turbidity is the same as that of the sample, which has been diluted to a convenient volume in a Nessler tube or similar comparison cylinder. The apparatus used in determining small amounts of titanium, lead, etc., is suitable for this test. In this case the glowing wire or filament of an incandescent light is viewed through the solutions, the brightness of the wire acting as a guide in matching the solutions.

### Sulphurous Acid in Acetic Acid

This is best detected by placing in a small flask about 20 cc. of the sample, adding 5 cc. of strong hydrochloric acid and about 3 grams of zinc and covering with a filter paper saturated with lead acetate. The blackening of the paper indicates  $\text{SO}_2$  in the sample (e.g., reduced to  $\text{H}_2\text{S}$  by the hydrogen generated by the zinc).

The sulphurous acid is best titrated with N/10 iodine solution, using starch indicator. 1 cc. N/10  $\text{I}_2$  = .0032 gr.  $\text{SO}_2$ .

### Hydrochloric Acid in Acetic Acid

Determined by the turbidity test as in case of sulphuric acid, silver nitrate solution being used to precipitate  $\text{AgCl}$ , and nitric acid substituted for hydrochloric acid.

### Metals in Acetic Acid

**Total Solids.** Ten to 100 grams of the acid is evaporated to dryness in a platinum dish. The residue contains the non-volatile solids.

## ACETATES

Two to 5 grams of the material is placed in a Kjeldahl flask connected by means of a condenser to a receiving flask containing half normal caustic. About 20 cc of 85 per cent phosphoric acid are added and about 150 cc. of water. Gentle heat is applied and gradually increased. About 100 cc. of the solution is distilled into the caustic. Additional hot water is added to the residue in the Kjeldahl flask and the distillation continued. This is repeated until about 800 cc. of solution has been distilled over. The  $\text{CO}_2$  is boiled out of the distillate, a reflux condenser being used to prevent loss of the acetic acid. If the solution is alkaline, a known



amount of acid is added and the  $\text{CO}_2$  boiled out. The excess acid is now titrated and the amount of acetic acid in the distillate calculated.

One cc. N/2 NaOH = 0.030015 gram  $\text{CH}_3\text{COOH}$ .

$\text{CH}_3\text{COOH} \times 1.3169 = \text{Ca}(\text{CH}_3\text{CO}_2)_2$ , or  $\times 1.3663 = \text{CH}_3\text{COONa}$ .

**Acetates of the Alkalies and Alkaline Earths.** In absence of other organic acids, nitrates, etc., a quick method is suggested by Sutton (Vol. Analy., X. Ed. p. 91). The salts are converted into carbonates by ignition and the residue titrated with normal acid.

One cc. N/1 acid = 0.06003 gram  $\text{CH}_3\text{COOH}$ .

### ACETIC ACID AT 15°

OUDEMANS

Specific Gravity.	Per Cent $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$	Specific Gravity.	Per Cent $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$	Specific Gravity.	Per Cent $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$	Specific Gravity.	Per Cent $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$
0.9992	0	1.0363	26	1.0623	51	1.0747	76
1.0007	1	1.0375	27	1.0631	52	1.0748	77
1.0022	2	1.0388	28	1.0638	53	1.0748	78
1.0037	3	1.0400	29	1.0646	54	1.0748	79
1.0052	4	1.0412	30	1.0653	55	1.0748	80
1.0067	5	1.0424	31	1.0660	56	1.0747	81
1.0083	6	1.0436	32	1.0666	57	1.0746	82
1.0098	7	1.0447	33	1.0673	58	1.0744	83
1.0113	8	1.0459	34	1.0679	59	1.0742	84
1.0127	9	1.0470	35	1.0685	60	1.0739	85
1.0142	10	1.0481	36	1.0691	61	1.0736	86
1.0157	11	1.0492	37	1.0697	62	1.0731	87
1.0171	12	1.0502	38	1.0702	63	1.0726	88
1.0185	13	1.0513	39	1.0707	64	1.0720	89
1.0200	14	1.0523	40	1.0712	65	1.0713	90
1.0214	15	1.0533	41	1.0717	66	1.0705	91
1.0228	16	1.0543	42	1.0721	67	1.0696	92
1.0242	17	1.0552	43	1.0725	68	1.0686	93
1.0256	18	1.0562	44	1.0729	69	1.0674	94
1.0270	19	1.0571	45	1.0733	70	1.0662	95
1.0284	20	1.0580	46	1.0737	71	1.0644	96
1.0298	21	1.0589	47	1.0740	72	1.0625	97
1.0311	22	1.0598	48	1.0742	73	1.0604	98
1.0324	23	1.0607	49	1.0744	74	1.0580	99
1.0337	24	1.0615	50	1.0746	75	1.0553	100
1.0350	25						

**CARBONIC ACID****Free Carbonic Acid in Aqueous Solution**

The method is based on the reaction



**Procedure.** An excess of standard barium hydroxide solution is added to the water containing the carbonic acid. Barium carbonate is precipitated as shown in the reaction above. The excess of  $\text{Ba}(\text{OH})_2$  is now titrated with standard hydrochloric acid, using phenolphthalein indicator.

1 cc. N/10  $\text{Ba}(\text{OH})_2$  or 1 cc. N/10  $\text{HCl}$  is equivalent to 0.0022 g.  $\text{CO}_2$ .

**Carbonic Acid Present as Bicarbonate**

**Reaction.**  $\text{NaHCO}_3 + \text{HCl} = \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$ .

**Procedure.** The solution is titrated with standard  $\text{HCl}$ , using methyl orange indicator.

1 cc. N/10  $\text{HCl} = 0.0044$  g.  $\text{CO}_2$ .

**Carbonic Acid Present as Carbonate**

**Reaction.**  $\text{Na}_2\text{CO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$ .

**Procedure.** The solution is titrated with standard  $\text{HCl}$ , using methyl orange indicator. Carbonates of barium, strontium, calcium and magnesium are titrated with an excess of hydrochloric acid and this excess determined with standard alkali.

1 cc. N/10  $\text{HCl} = 0.0022$  g.  $\text{CO}_2$ .

**CITRIC ACID**

The free acid may be titrated with sodium hydroxide, using phenolphthalein indicator. One cc. N/1 alkali = 0.07 gram crystallized citric acid.

**VOLUMETRIC DETERMINATION OF OXALIC ACID****Permanganate Method**

About 3 grams of the oxalic acid or its salt are dissolved in 200 cc. of  $\text{CO}_2$  free water and 50 cc. 2N sulphuric acid added. The solution is heated to about  $70^\circ \text{C}$ . and titrated with standard, normal solution of potassium permanganate, to a faint pink, persisting for three minutes.

1 cc. N/ $\text{KMnO}_4$  = 0.04501 g.  $\text{H}_2\text{C}_2\text{O}_4$  or 0.06302 g.  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

The acid may also be titrated with standard caustic solution. Titration is made in a hot solution, using phenolphthalein indicator.

**DETERMINATION OF PHENOL (CARBOLIC ACID)**

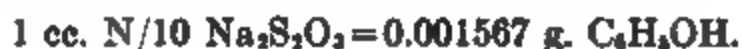
Bromine reacts with an aqueous solution of phenol decomposing it to the water insoluble tribromophenol and forming hydrobromic acid as shown in the reaction



The excess of bromine is determined by adding potassium iodide solution and determining the liberated iodine by titration with standard thiosulphate. The method is applicable only to pure preparations of carbolie acid.

**Reagent. Standard Bromine.** A solution of free bromine in water cannot be kept. The reagent may be prepared, however, by adding a definite amount of bromate to a bromide solution, which on acidification, will liberate a definite amount of bromine according to the reaction  $\text{KBrO}_3 + 5\text{KBr} + 6\text{HCl} = 3\text{Br}_2 + 6\text{KCl} + 3\text{H}_2\text{O}$ . The acid is added only to the portions of the reagent used for the tests. In preparing a N/10 solution 2.784 grams of pure dry potassium bromate and 10 grams of potassium bromide are dissolved in a little water and diluted to 1000 cc.

**Procedure.** 0.5 gram of phenol is dissolved in a little water and diluted to 1000 cc. To 100 cc. of this, equivalent to 0.05 g. of sample are added (in a stoppered bottle) 50 cc. of the bromate solution and the mixture shaken. 5 cc. of strong HCl are now added, the solution again shaken and after 15 minutes 2 grams of potassium iodide are added. The liberated iodine is titrated in presence of starch solution with N/10 thiosulphate.



### TARTARIC ACID

Tartaric acid, cream of tartar, Rochelle salt, tartar emetic, normal potassium tartrate, iron tartrate and other salts of tartaric acid are obtained from the residues of wine manufacture. The raw materials consist of lees, tartars, calcium tartrate. Tartaric acid is present in these residues in the form of potassium hydrogen tartrate (bitartrate of potassium) or as normal calcium tartrate. In the examination of the raw material for its evaluation total tartaric acid and that present as bitartrate are determined.

#### Estimation of Acid Potassium Tartrate—Oulman's Method

**Procedure.** 3.76 grams of the powdered tartar is placed in a liter flask, 750 cc. of water added, the solution heated to boiling and boiled for 4 to 5 minutes. Prolonged boiling is avoided, as changes may occur which would cause error in results. The flask is filled to the mark and allowed to cool. After readjusting to exactly one liter the solution is filtered through a dry filter and 500 cc. of this evaporated to dryness on the water-bath in a porcelain casserole. 5 cc. of water is added to moisten this residue and 100 cc. of 95 per cent alcohol added on cooling. After standing half an hour the alcohol is decanted through a dry filter, allowed to drain and any potassium bitartrate on the filter is washed back into the dish with hot water. The solution is made up to about 100 cc. and titrated hot with N/5 KOH. A correction of 0.2 cc. is added for the loss of bitartrate in the alcohol.

**Estimation of Total Tartaric Acid. Goldenberg Method, 1907**

**Procedure.** Six grams of the sample containing more than 45 per cent of tartaric acid or 12 grams if it contains less than 45 per cent are added to 18 cc. of hydrochloric acid (sp.gr. 1.1) and the mixture stirred 10 minutes. This is now transferred to a 200 cc. measuring flask and distilled water added to the mark. The well mixed solution is now filtered through a dry filter into a beaker. 100 cc. is pipetted out and added to 10 cc. of a solution of potassium carbonate containing 66 grams of the anhydrous salt per 100 cc. in a 300 cc. beaker. The breaker is covered by a clock glass and the solution boiled gently for twenty minutes; the calcium carbonate precipitates in a crystalline form during this heating. The solution is transferred to a 200 cc. measuring flask, made up to mark after cooling, and filtered through a dry filter.

100 cc. of the filtrate is evaporated in a porcelain casserole (or pyrex beaker) on the water bath until the volume is about 15 cc. To the hot solution 3.5 cc. of glacial acetic acid are added gradually with constant stirring and the mixture stirred for 5 minutes more after the addition. After standing 10 minutes 100 cc. of 95 per cent alcohol are added and the mixture again stirred 5 minutes. Upon settling 10 minutes the precipitated bitartrate is filtered off, suction being applied. The precipitate is washed with alcohol until free of acid. (Test 30 cc. This should require the same titration with N/5 alkali with phenolphthalein indicator as 30 cc. of the alcohol used in the washing.) The precipitate on the filter is washed into a porcelain dish with 200 cc. of hot water and titrated hot with N/5 potassium or sodium hydroxide, using litmus paper as indicator.

The alkali is standardized against pure potassium hydrogen tartrate.

**Corrections.** Deduct 0.3 per cent for material containing less than 45 per cent tartaric acid, 0.3 per cent for raw material containing 45-60 per cent and 0.2 per cent for material containing 60-70 per cent. No correction is made for better grades of material.

**Impurities in Tartaric Acid**

**Iron and Alumina (alum.).** These are determined in the ash of the ignited product, the ash being dissolved in hydrochloric acid.  $P_2O_5$  may also be determined in this ash.

**Arsenic.** This may be determined by the Gutzeit Method. (See chapter on Arsenic in Volume I.)

**Lead.** This is determined by the colorimetric procedure given on page 281, Vol. I.

**Free Sulphuric Acid in Tartaric Acid Liquors.** The solution 10 cc. or more is treated with ten times its volume of alcohol, and after settling overnight the mixture is filtered. Sulphuric acid is determined in the alcohol filtrate in the usual way.

## ALKALIES

## ANALYSIS OF SODIUM HYDROXIDE

Commercial caustic soda, purchased in blocks packed in iron drums, should be sampled with care. The hydroxide sets first on the outside, so that the impurities segregate towards the core of the block. In order to get a representative sample different sections of the block should be tapped. The material takes up moisture and carbon dioxide from the air, so that the surface of the sample should be removed before weighing. The weighing and dissolving of the sample should be done as rapidly as possible.

## Procedure

Ten grams of the hydroxide are dissolved in water and the solution made up to exactly 500 cc. Aliquots of this solution are taken for the following determinations.

**Total Alkali.** Fifty cc. of the caustic solution, equivalent to 1 gram of the solid, are titrated with  $N/H_2SO_4$  in presence of methyl orange indicator, until the faint pink end-point is obtained.

1 cc.  $N/H_2SO_4 = .031$  grams of  $Na_2O$  (total alkali actual).

**NOTE.** In the New York and Liverpool test  $N/H_2SO_4$  value is .032 g.  $NaOH$  per cc.

**Sodium Hydroxide.** Fifty cc. of the sample is treated with 100 cc. of 10%  $BaCl_2$  solution and the  $NaOH$  then titrated with  $N/H_2SO_4$  in presence of phenolphthalein indicator.

1 cc.  $N/H_2SO_4 = .04$  gram  $NaOH$ .

**Sodium Carbonate.** Multiply the difference between the total alkali titration and the titration for  $NaOH$  by .053 the result is grams  $Na_2CO_3$ .

**Alternative Methods. Sodium Hydroxide and Sodium Carbonate.** Carbon dioxide is readily picked up by  $NaOH$  so that it is invariably present in caustic soda forming sodium carbonate. The carbonate and hydrate may be determined in the same solution as follows.

Fifty cc. of the sample equivalent to one gram of the solid, are titrated with normal  $H_2SO_4$  in presence of phenolphthalein, until the pink color just disappears. This occurs when all of the sodium hydroxide is neutralized and the carbonate has been converted to bicarbonate. This titration may be recorded as cc. *A*.

Methyl orange is now added and the titration continued until the yellow color changes to pink. This titration is recorded as cc. *B*.

Then  $NaOH = (A - B) \times 0.04$  and  $Na_2CO_3 = 2B \times 0.053$ .

## Determination of Impurities

**Sodium Chloride.** This may be determined on 25 to 50 cc. (0.5–1 gram) of the above solution by Volhard's method described in Vol. I, page 149, or the method for  $NaCl$  in soda ash, page 1064, this volume.

1 cc.  $N/20 AgNO_3 = 0.002923$  gram  $NaCl$ .

**Sodium Sulphate.** Fifty cc. of the solution equivalent to 1 gram of the solid are acidified with hydrochloric acid ( $H_2SO_4$  free) and the sulphate precipitated from a boiling solution by addition of 10%  $BaCl_2$  solution according to the standard procedure.

$BaSO_4 \times 0.6086 = Na_2SO_4$ .

The following determinations are seldom required.

**Sodium Silicate.** 10 grams of the sample are dissolved in about 100 cc. of water and the solution acidified with hydrochloric acid. After evaporation to dryness the residue is taken up with water. Silica remains insoluble and is filtered off, washed, ignited and weighed.  $\text{SiO}_2 \times 2.0282 = \text{Na}_2\text{SiO}_2$ .

**Sodium Aluminate.** The water extract from silica contains the alumina as soluble chloride.  $\text{Al}(\text{OH})_3$  may be precipitated with ammonia according to the standard procedure, then filtered off, washed, ignited and weighed as  $\text{Al}_2\text{O}_3$ .  $\text{Al}_2\text{O}_3 \times 1.6067 = \text{Na}_2\text{Al}_2\text{O}_4$ .

**Insoluble Matter.** 100 grams of the material is dissolved in a liter of water, phenolphthalein indicator is added and the solution almost neutralized with hydrochloric acid, the solution should be slightly alkaline. The sample is filtered and the residue of sand,  $\text{Fe}_2\text{O}_3$ , etc., weighed as insoluble matter. Caustic solutions attack filter paper so that it is advisable to partly neutralize the free alkali before filtration.

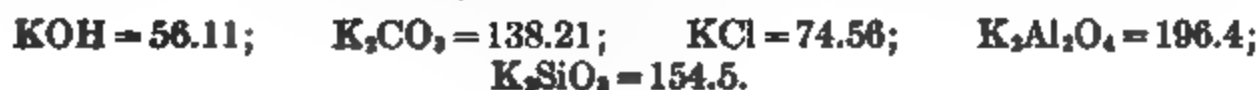
**Water.** 5 to 10 grams of the hydroxide are placed in a small Erlenmeyer flask, whose weight is known, a funnel is placed in the neck of the flask to prevent loss of the material and to prevent its absorbing carbon dioxide from the air. After placing in a sand bath the material is kept at about  $150^\circ \text{C}$ . for about four hours. It is now allowed to cool, the funnel remaining in the flask, and the loss of weight determined.

### Determination of Strength of Caustic Liquors by the Hydrometer

The specific gravity of the liquor is taken by the hydrometer exactly as in case of acids. The strength of the liquor is ascertained by reference to the table on Sodium Hydroxide, page 1068.

### POTASSIUM HYDROXIDE

Analysis of potassium hydroxide is similar to that of sodium hydroxide. The following molecular weights will be of use in the calculations:



## ANALYSIS OF SODIUM CARBONATE

## Soda Ash

Sodium carbonate,  $\text{Na}_2\text{CO}_3$  (soda ash), and two forms with water of crystallization crystal carbonate,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  and soda crystals or washing soda,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , are commonly known. In the analysis of soda ash the customary demand is for total alkali, sodium carbonate, sodium bicarbonate, and sodium chloride. In a complete analysis, including the insoluble residue iron,  $\text{Fe}_2\text{O}_3$ , sodium sulphate, sodium thio-sulphate, sodium sulphite, sodium sulphide, sodium silicate, sodium hydroxide, alumina, and water may be required.

## Procedure

**Total Alkali,  $\text{Na}_2\text{O}$ .** Five grams of the soda ash are dissolved in 50 cc. of distilled water, preferably in an Erlenmeyer flask, with a funnel, the stem extending in the neck of the flask. 95 cc. of normal sulphuric acid are added and the solution boiled gently to expel the  $\text{CO}_2$ , the funnel prevents loss during boiling. After cooling, methyl orange indicator is added and the titration completed. The end point is a faint pink color.

1 cc.  $\text{N}/\text{H}_2\text{SO}_4 = .031$  gram  $\text{Na}_2\text{O}$ .

NOTE. "New York and Liverpool test" the value of 1 cc.  $\text{N.H}_2\text{SO}_4 = .032$  g.  $\text{Na}_2\text{O}$ .

**Sodium Bicarbonate,  $\text{NaHCO}_3$ .** Five grams of the soda ash are dissolved in 100 cc. of water and the solution titrated with normal sodium hydroxide until a drop of the solution on a spot plate produces an immediate dark color with a drop of silver nitrate.

1 cc.  $\text{N}/\text{NaOH} = .084$  gram  $\text{NaHCO}_3$ .

**Sodium Carbonate.** Deduct the cc. titration of  $\text{NaOH}$  for  $\text{NaHCO}_3$  from the cc.  $\text{H}_2\text{SO}_4$  titration for  $\text{Na}_2\text{O}$ , the difference in cc. multiplied by .053 = gram  $\text{Na}_2\text{CO}_3$ .

**Sodium Chloride.** Two grams of the ash by the Solvay process or 5 grams by the Leblanc process are dissolved in 50 to 100 cc. of distilled water and 5 cc. of colorless  $\text{HNO}_3$  (sp.gr., 1.42) added. 2 cc. of ferric ammonium sulphate are used as indicator, followed by a few drops of  $\text{N}/20$   $\text{KCNS}$  solution, the exact amount of this being noted. The chloride is now titrated with  $\text{N}/20$   $\text{AgNO}_3$  solution until the color is just destroyed, then 1 cc. in excess is added. The precipitate is filtered off and washed. The filtrate and washings are now titrated with  $\text{N}/20$   $\text{KCNS}$  to a permanent pink color.

The total cc.  $\text{KCNS}$  is deducted from the cc.  $\text{AgNO}_3$  added and the difference multiplied by 0.002923 gram  $\text{NaCl}$ .

NOTE. See Volhard's method for chloride in Vol. I, page 149.

In addition to the above determinations the following may be desired:

**Insoluble Matter.** Fifty grams of the soda ash are dissolved in about 500 cc. of water the insoluble matter allowed to settle, the clear solution decanted through a double filter, which has been weighed, and finally the residue washed onto the filter. The residue and filters are dried at  $100^\circ \text{C}$ . and weighed.

Weight minus tare of filters multiplied by 100 = per cent insoluble matter.

<sup>1</sup> Ferric ammonium sulphate 6 per cent solution made by dissolving the salt in 50 parts of water to 6 parts of salt and adding an equal volume of colorless nitric acid.

<sup>2</sup>  $\text{N}/20$  silver nitrate contains 8.495 g.  $\text{AgNO}_3$  per liter. Standardize against pure  $\text{NaCl}$ .

<sup>3</sup>  $\text{N}/20$  potassium thiocyanate,  $\text{KCNS}$ , contains 4.86 grams of the salt per liter. The solution should be standardized against the silver nitrate solution.

**Iron, Alumina, Lime and Magnesia.** These are determined in the insoluble residue by dissolving out by means of dilute hydrochloric acid. The residue consists of *sand and carbonaceous matter*. Iron and alumina are precipitated out together by addition of ammonia according to the standard procedure, and determined as oxides,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ . Iron may be determined in this residue by dissolving in  $\text{HCl}$  and titrating with stannous chloride according to the procedure given in Vol. I, page 373. Alumina is obtained by difference. Lime and magnesia will be found in the filtrates from iron and alumina precipitates. Calcium is thrown out as an oxalate and magnesium as a phosphate and determined as usual.

**Sodium Sulphate.** Dissolve 5 to 10 grams in dilute  $\text{HCl}$  and add  $\text{BaCl}_2$ . The precipitate  $\text{BaSO}_4$  is washed and ignited as usual.

$$\text{BaSO}_4 \times 0.6086 = \text{gram Na}_2\text{SO}_4$$

**Sodium Sulphite.** 5 grams are dissolved in water and the solution acidified with acetic acid. Starch solution is added and the sulphite titrated with  $\text{N}/10$  iodine until the blue color appears.

$$1 \text{ cc. } \text{N}/10 \text{ I} = 0.006303 \text{ gram Na}_2\text{SO}_3$$

**Sodium Silicate.** Ten grams of the soda ash are treated with an excess of  $\text{HCl}$  and the solution evaporated to dryness, the silica dehydrated at  $110^\circ \text{C}$ . After leaching with water the insoluble  $\text{SiO}_2$  is determined by filtering off and igniting by the standard procedure.

$$\text{SiO}_2 \times 2.0282 = \text{Na}_2\text{SiO}_3$$

**Sodium Sulphide.** This may be estimated by titration with an ammoniacal solution of silver nitrate (13.81 g. silver per liter = 1 cc. = .005 g.  $\text{Na}_2\text{S}$ ). Add the reagent until no further precipitation occurs of  $\text{Ag}_2\text{S}$ . To get a good end point the solution is filtered just before this point is reached and the titration completed. See also chapter on Sulphur, Volume I.

**Loss on Ignition.** The sample 10 grams is ignited at a temperature slightly below  $300^\circ \text{C}$ . The loss is due largely to water and organic matter.

## MODIFIED SODAS

### Causticized Ash

The determination of total alkali, sodium hydroxide and sodium carbonate are generally required. 20 grams of the sample are dissolved in water and the solution made to one liter. Aliquot portions of this solution are taken for analysis.

**Total Alkali.** The determination is similar to that described for soda ash on page 1064 the test being made on 50 cc. of the solution equivalent to 1 gram of sample. It is advisable to add a slight excess of  $\text{N}/\text{H}_2\text{SO}_4$  and titrate back with  $\text{N}/\text{NaOH}$  using methyl orange indicator. The end point is a faint pink.

$$1 \text{ cc. } \text{N}/\text{H}_2\text{SO}_4 = 0.031 \text{ gram Na}_2\text{O}$$

**Sodium Hydroxide.** Fifty cc. of the sample equivalent to 1 gram of the solid is taken. The analysis is the same as that described for determining  $\text{NaOH}$  in caustic soda on page 1062.

**Sodium Carbonate.** The difference between the acid titration for total alkali and that for sodium hydroxide is multiplied by 0.053 = gram  $\text{Na}_2\text{CO}_3$

### Washing Soda (Neutral Soda)

The determination of total alkali, sodium carbonate, sodium bicarbonate, and sodium chloride are generally required. The method of analysis is the same as has been described under soda ash. See page 1064.



## ESTIMATION OF THE CARBONATES AND HYDRATES OF POTASSIUM AND SODIUM WHEN TOGETHER IN SOLUTION<sup>1</sup>

**Procedure.** A measured volume of the solution is titrated, using phenolphthalein as indicator. The acid used is equivalent to all of the hydrate and half the carbonate; methyl orange is now added and the titration completed; the additional amount of the acid used is equivalent to half the carbonate, therefore the amount of acid required for the carbonates and for the hydrates can be calculated from these figures.

The fully neutralized solution is evaporated to dryness and the residue weighed. The result is the weight of the mixed sulphates, due to the carbonates and hydrates of potassium and soda in the solution.

Calculate the total acid required to its equivalent of potassium sulphate, subtract from this result the weight of the mixed sulphates, and the difference is due to the sodium sulphate in the mixed sulphates, owing to the difference in the molecular weights of potassium sulphate and sodium sulphate. The whole of the acid used has been calculated to potassium sulphate, and as the acid was neutralized by carbonates and hydrates, it is evident the proportion of total sulphate, due to the carbonates and hydrates, is equivalent to the amount of the acid used for each respectively; therefore the proportion of the above obtained difference due to the carbonates and the hydrates respectively is also proportional to the amount of acid used for each.

**Example.** A solution of the mixed carbonates and hydrates of potassium and sodium required:

(40 cc. NaOH : 40 cc. KOH) 80 cc. of acid to neutralize the hydrates.

(10 cc. Na<sub>2</sub>CO<sub>3</sub> : 10 cc. K<sub>2</sub>CO<sub>3</sub>) 20 cc. of acid to neutralize the carbonates.

100 cc. total acid required to neutralize the solution.

Total acid 100 cc. calculated to K<sub>2</sub>SO<sub>4</sub> = 0.87 gram.

Total neutralized solution evaporated to dryness (K<sub>2</sub>SO<sub>4</sub> + Na<sub>2</sub>SO<sub>4</sub>) = 0.79 gram.

Difference due to Na<sub>2</sub>SO<sub>4</sub> in weighed sulphates = 0.08 gram.

(K<sub>2</sub>SO<sub>4</sub> - Na<sub>2</sub>SO<sub>4</sub>) : Na<sub>2</sub>SO<sub>4</sub> :: Diff :

32 : 142 :: 0.08 : 0.355 Na<sub>2</sub>SO<sub>4</sub> present in the mixed sul-

phates.

And the mixed sulphates 0.79 gram - 0.355 = 0.435 K<sub>2</sub>SO<sub>4</sub> present in the mixed sulphates.

Therefore the mixed sulphates consist of Na<sub>2</sub>SO<sub>4</sub> 0.355 gram, K<sub>2</sub>SO<sub>4</sub> 0.435 gram.

The proportion of the acid used for the hydrates is 80/100 and for the carbonates is 20/100.

Therefore the proportion of the difference (0.08) due to Na<sub>2</sub>SO<sub>4</sub> from the hydrate NaOH is  $0.08 \times 80/100 = 0.064$ . For the carbonates  $= 0.08 \times 20/100 = 0.016$ .

By the above ratios 32 : 142 :: 0.064 : 0.284 Na<sub>2</sub>SO<sub>4</sub> from NaOH = 40 cc. N/10 acid. 32 : 142 :: 0.016 : 0.071 Na<sub>2</sub>SO<sub>4</sub> from Na<sub>2</sub>CO<sub>3</sub> = 10 cc. acid.

<sup>1</sup>W. A. Bradbury and F. Owen. C. N., 107, 2778, 85 (Feb. 21, 1913).

80 cc. acid used for the hydrates = 0.696  $K_2SO_4$   
 0.284  $Na_2SO_4$  from the  $NaOH$  = 0.348  $K_2SO_4$   
 Difference =  $K_2SO_4$  from  $KOH$  = 0.348 = 40 cc. N/10 acid.  
 20 cc. acid used for the carbonates = 0.174.  
 0.071  $Na_2SO_4$  from the  $Na_2CO_3$  = 0.087.  
 Difference =  $K_2SO_4$  from  $K_2CO_3$  = 0.087 = 10 cc. acid.

The figures correspond with the quantities taken.

80 cc. of acid to neutralize the hydrates.

20 cc. of acid to neutralize the carbonates.

$$Na_2SO_4 = 0.355 \left\{ \begin{array}{l} NaOH \ 0.284 = 40 \text{ cc. acid} \\ Na_2CO_3 \ 0.071 = 10 \text{ cc. acid} \end{array} \right\} 80 \text{ cc. acid.}$$

$$K_2SO_4 = 0.435 \left\{ \begin{array}{l} KOH \ 0.348 = 40 \text{ cc. acid} \\ K_2CO_3 \ 0.087 = 10 \text{ cc. acid} \end{array} \right\} 20 \text{ cc. acid}$$

Totals    0.790                      0.790(a)100

Calculate these sulphates to the corresponding hydrates and carbonates.

## DETERMINATION OF SODIUM BICARBONATE AND SODIUM CARBONATE IN PRESENCE OF ONE ANOTHER

Five grams of the sample are dissolved in  $CO_2$ -free water, and the solution made up to exactly 250 cc. in a measuring flask. Aliquot portions of 25 cc., equivalent to 0.5 gram, are taken for analysis. The sample taken is titrated with N/5 hydrochloric acid in presence of phenolphthalein indicator (2-3 drops). The cc. titration recorded as "A," represents one half of the sodium carbonate present. Methyl orange indicator is now added (2-3 drops) and the titration with the acid continued until the solution turns faintly pink. The remaining carbonate and all of the bicarbonate are now titrated. The cc. titration are recorded as B.

$$2A \times 0.0106 = Na_2CO_3 \text{ and } B - A \times 0.0168 = NaHCO_3.$$

The author desires to acknowledge his indebtedness to Dr. W. B. Hicks, Chief of the Analytical Department, The Solvay Process Company, for his review of the section on Alkalies.

## SODIUM HYDROXIDE SOLUTION AT 15°

LUNGE

Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	Per Cent Na <sub>2</sub> O.	Per Cent NaOH.	1 Liter contains Grams	
					Na <sub>2</sub> O.	NaOH.
1.007	1.0	1.4	0.47	0.61	4	6
1.014	2.0	2.8	0.93	1.20	9	12
1.022	3.1	4.4	1.55	2.00	16	21
1.029	4.1	5.8	2.10	2.70	22	28
1.036	5.1	7.2	2.60	3.35	27	35
1.045	6.2	9.0	3.10	4.00	32	42
1.052	7.2	10.4	3.60	4.64	37	49
1.060	8.2	12.0	4.10	5.29	43	56
1.067	9.1	13.4	4.55	5.87	49	63
1.075	10.1	15.0	5.08	6.55	55	70
1.083	11.1	16.6	5.67	7.31	61	79
1.091	12.1	18.2	6.20	8.00	68	87
1.100	13.2	20.0	6.73	8.68	74	96
1.108	14.1	21.6	7.30	9.42	81	104
1.116	15.1	23.2	7.80	10.06	87	112
1.125	16.1	25.0	8.50	10.97	96	123
1.134	17.1	26.8	9.18	11.84	104	134
1.142	18.0	28.4	9.80	12.64	112	144
1.152	19.1	30.4	10.50	13.55	121	156
1.162	20.2	32.4	11.14	14.37	129	167
1.171	21.2	34.2	11.73	15.13	137	177
1.180	22.1	36.0	12.33	15.91	146	183
1.190	23.1	38.0	13.00	16.77	155	200
1.200	24.2	40.0	13.70	17.67	164	212
1.210	25.2	42.0	14.40	18.58	174	225
1.220	26.1	44.0	15.18	19.58	185	239
1.231	27.2	46.2	15.96	20.59	196	253
1.241	28.2	48.2	16.76	21.42	208	266
1.252	29.2	50.4	17.55	22.64	220	283
1.263	30.2	52.6	18.35	23.67	232	299
1.274	31.2	54.8	19.23	24.81	245	316
1.285	32.2	57.0	20.00	25.80	257	332
1.297	33.2	59.4	20.80	26.83	270	348
1.308	34.1	61.6	21.55	27.80	282	364
1.320	35.2	64.0	22.35	28.83	295	381
1.332	36.1	66.4	23.20	29.93	309	399
1.345	37.2	69.0	24.20	31.22	326	420
1.357	38.1	71.4	25.17	32.47	342	441
1.370	39.2	74.0	26.12	33.69	359	462
1.383	40.2	76.6	27.10	34.96	375	483
1.397	41.2	79.4	28.10	36.25	392	504
1.410	42.2	82.0	29.05	37.47	410	528
1.424	43.2	84.8	30.03	38.80	428	553
1.438	44.2	87.0	31.00	39.99	446	575
1.453	45.2	90.0	32.10	41.41	466	602
1.468	46.2	93.6	33.20	42.83	487	629
1.483	47.2	96.6	34.40	44.38	510	658
1.498	48.2	99.6	35.70	46.15	535	691
1.514	49.2	102.8	36.90	47.60	559	721
1.530	50.2	106.0	38.00	49.02	581	750

AQUA AMMONIA  
According to W. C. FERGUSON

Degrees Baumé.	Sp. Gr. 60° F.	Per Cent NH <sub>3</sub> .	Degrees Baumé.	Sp. Gr. 60° F.	Per Cent NH <sub>3</sub> .	Degrees Baumé.	Sp. Gr. 60° F.	Per Cent NH <sub>3</sub> .
10.00	1.0000	.00	16.50	.9550	11.18	23.00	.9150	23.52
10.25	.9982	.40	16.75	.9540	11.64	23.25	.9135	24.01
10.50	.9964	.80	17.00	.9524	12.10	23.50	.9121	24.50
10.75	.9947	1.21	17.25	.9508	12.56	23.75	.9106	24.99
11.00	.9930	1.62	17.50	.9492	13.02	24.00	.9091	25.48
11.25	.9912	2.04	17.75	.9475	13.49	24.25	.9076	25.97
11.50	.9894	2.46	18.00	.9459	13.96	24.50	.9061	26.46
11.75	.9876	2.88	18.25	.9444	14.43	24.75	.9047	26.95
12.00	.9859	3.30	18.50	.9428	14.90	25.00	.9032	27.44
12.25	.9842	3.73	18.75	.9412	15.37	25.25	.9018	27.93
12.50	.9825	4.16	19.00	.9396	15.84	25.50	.9003	28.42
12.75	.9807	4.59	19.25	.9380	16.32	25.75	.8989	28.91
13.00	.9790	5.02	19.50	.9365	16.80	26.00	.8974	29.40
13.25	.9773	5.45	19.75	.9349	17.28	26.25	.8960	29.89
13.50	.9756	5.88	20.00	.9333	17.76	26.50	.8946	30.38
13.75	.9739	6.31	20.25	.9318	18.24	26.75	.8931	30.87
14.00	.9722	6.74	20.50	.9302	18.72	27.00	.8917	31.36
14.25	.9705	7.17	20.75	.9287	19.20	27.25	.8903	31.85
14.50	.9689	7.61	21.00	.9272	19.68	27.50	.8889	32.34
14.75	.9672	8.05	21.25	.9256	20.16	27.75	.8875	32.83
15.00	.9655	8.49	21.50	.9241	20.64	28.00	.8861	33.32
15.25	.9639	8.93	21.75	.9225	21.12	28.25	.8847	33.81
15.50	.9623	9.38	22.00	.9211	21.60	28.50	.8833	34.30
15.75	.9605	9.83	22.25	.9195	22.08	28.75	.8819	34.79
16.00	.9589	10.28	22.50	.9180	22.56	29.00	.8805	35.28
16.25	.9573	10.73	22.75	.9165	23.04			

ALLOWANCE FOR TEMPERATURE

The coefficient of expansion for ammonia solutions, varying with the temperature, correction must be applied according to the following table:

Corrections to be Added for Each Degree Below 60° F.			Corrections to be Subtracted for Each Degree Above 60° F.			
Degrees Baumé.	40° F.	50° F.	70° F.	80° F.	90° F.	100° F.
14° B <sub>é</sub>	.015° B <sub>é</sub>	.017° B <sub>é</sub>	.020° B <sub>é</sub>	.022° B <sub>é</sub>	.024° B <sub>é</sub>	.026° B <sub>é</sub>
16°	.021 "	.023 "	.026 "	.028 "	.030 "	.032 "
18°	.027 "	.029 "	.031 "	.033 "	.035 "	.037 "
20°	.033 "	.036 "	.037 "	.038 "	.040 "	.042 "
22°	.039 "	.042 "	.043 "	.045 "	.047 "	
26°	.053 "	.057 "	.057 "	.059 "		

## ANALYSIS OF AQUA AMMONIA

Details for the complete analysis of crude ammoniacal liquor will be found in Volume I on pages 344-345.

The per cent ammonia in a solution free from other substances may be determined with a fair degree of accuracy by determining the specific gravity of the solution by means of the hydrometer. Since the specific gravity of aqua ammonia is less than 1, hydrometers graduated for measuring liquids lighter than water are used. The formula for 1 degree Baume =  $(140/\text{sp.gr.}) - 130$ . Reference is made to the table on Aqua Ammonia.

Provided no other basic constituent is present, free ammonia in solution is best determined by direct titration with an acid in presence of methyl orange or methyl red as indicator.

**Procedure.** About 10 grams of the solution in a weighing bottle with glass stopper is introduced into an 800-cc. Erlenmeyer flask containing about 200 cc. of water and sufficient  $\frac{1}{2}$  normal sulphuric acid to combine with the ammonia and about 10 cc. in excess. The flask is stoppered and warmed gently. This forces out the stopper in the weighing bottle, the ammonia combining with the acid. Upon thorough mixing, the solution is cooled, and the excess of acid is titrated with half normal caustic.

One cc.  $\frac{1}{2}$  N.  $\text{H}_2\text{SO}_4$  = 0.0085 gram  $\text{NH}_3$ .

Factor.  $\text{H}_2\text{SO}_4 \times 0.3473 = \text{NH}_3$ .

**NOTE.** The aqua ammonia exposed to the air will lose ammonia, hence the sample should be kept stoppered. This loss of ammonia is quite appreciable in strong ammoniacal solutions.

## ANALYSIS OF ALLOYS

JOHN C. OLSEN<sup>1</sup> AND WILLIAM B. PRICE<sup>2</sup>

**Difficulty of Complete Separation of Elements.** As the great majority of the substances with which the chemist is called upon to deal are complex rather than simple, a careful study of the separation of the elements is of the greatest importance. Only by the closest attention to details can success be attained in the analysis of complex substances. The importance of testing precipitates for impurities and the solution for unprecipitated portions of an element cannot be too strongly urged. Only in this manner can the accuracy of an analysis be assured.

**Limit of Accuracy in Analysis.** If a complete analysis is made the sum of all the constituents must be very close to 100%. A summation which is within .5% can generally be obtained if the analysis is conducted with care and reliable methods are used. In general the analysis of an unknown substance should be conducted in duplicate. If the duplicate results do not agree within .2 or at most .3%, a third analysis should be made. As the error of most determinations is at least .1%, it is unnecessary to calculate results to more than hundredths of per cent. As the error in each determination of the analysis of a given substance may be either plus or minus, the practice of dividing the difference between the summation and 100% among the various determinations is not justifiable.

It is in some cases possible to analyze a substance in such a manner that the results are accurate to the hundredth of a per cent. Such results may be computed to the .001 of a per cent. This practice is common in the analysis of metals. Large quantities of the metal are taken, so that considerable quantities of the impurities which are present in small amounts are obtained for determination. The results may then be accurate to the hundredth of a per cent. This does not imply a higher degree of accuracy in the determination of a given element than .1 of a per cent. For example, if iron were present in copper to the extent of .5%, a determination of the iron which is accurate to .01% of the impure copper would represent an error of  $\frac{1}{50}$  of the amount of iron present in the copper. In giving the results of such analyses the percentage of the main constituent is obtained by difference, so that the summation is exactly 100%.

<sup>1</sup> Professor of Chemical Engineering Polytechnic Institute, Brooklyn, N. Y.

<sup>2</sup> Chief chemist and metallurgist, Scovill Manufacturing Co., Waterbury, Conn.

## Solution of Alloys and Outline of Separation

Among the solvents used may be mentioned nitric acid, aqua regia, sulphuric acid, fusion with acid fluxes.

## Nitric Acid Method

Treat one or more grams of the alloy filings or drillings with concentrated  $\text{HNO}_3$  or  $\text{HNO}_3$  1 : 1 until the metal is completely decomposed or in solution, adding water if necessary to assist solution.

- (a) If the metal dissolves, antimony and tin are absent; omit their tests.  
 (b) If the metal forms a turbid solution, antimony and tin may be present. To a portion, add several volumes of water and boil. (c) If a clear solution is formed treat the entire solution in the same way, and omit tests for Sn and Sb.  
 (c) If the residue is insoluble, Sb and Sn are indicated, evaporate the entire solution to dryness, gently ignite to expel water, add  $\text{HNO}_3$ , heat, dilute and filter. If the filtrate is turbid, repeat the filtration until clear.

<p><b>Precipitate.</b>—<math>\text{SnO}_2</math>; <math>\text{Sn}_2(\text{PO}_4)_4</math>; <math>\text{Sb}_2\text{O}_3</math>, all white and traces of the copper group metals.          a. Digest from 10 to 20 minutes with strong <math>\text{K}_2\text{S}</math>, <math>\text{Na}_2\text{S}</math> or <math>(\text{NH}_4)_2\text{S}</math> solution and filter.          b. Melt with <math>\text{Na}_2\text{CO}_3</math> and sulphur, cool, digest with water, and filter.</p>	<p><b>Filtrate.</b>—Contains the <math>\text{H}_2\text{S}</math> group (without tin and antimony) and <math>(\text{NH}_4)_2\text{S}</math> group.          Add from 1 to 3 cc. of concentrated <math>\text{H}_2\text{SO}_4</math> and evaporate to fumes, cool, dilute and filter.</p>
<p><b>Precipitate.</b>—Traces of copper group. If Sn, Sb in solution sufficient in quantity, dissolve in <math>\text{HNO}_3</math>; add <math>\text{HCl}</math> and filter.          to filtrate containing <math>(\text{NH}_4)_2\text{S}</math> group.          a. Analyze the precipitated sulphides.          b. Test the filtrate for phosphates.</p>	<p><b>Precipitate.</b>—<math>\text{PbSO}_4</math>, white. Treat with <math>\text{NH}_4\text{C}_2\text{H}_3\text{O}_2</math> (without Sn, Sb, and solution, filter, and add <math>\text{K}_2\text{CrO}_4</math>. A yellow precipitate in <math>(\text{NH}_4)_2\text{S}</math> group.          low precipitate in <math>(\text{NH}_4)_2\text{S}</math> group.          soluble in <math>\text{KOH}</math>. Into a portion of the solution pass in <math>\text{H}_2\text{S}</math>. A precipitate shows the presence of the <math>\text{H}_2\text{S}</math> group metals.</p>

- a. If the  $\text{H}_2\text{S}$  group is not present, as shown by a test on a portion of the solution, make a test for the  $(\text{NH}_4)_2\text{S}$  group.  
 b. If the  $\text{H}_2\text{S}$  group is present, precipitate the metals with  $\text{H}_2\text{S}$ , filter and wash.

<p><b>Precipitate.</b>—Contains the <math>\text{H}_2\text{S}</math> group, sulphides (without lead, tin and antimony).          If mercury is present use <math>(\text{NH}_4)_2\text{S}</math> to separate the sub-groups.          If mercury is absent digest the precipitate with 20 per cent <math>\text{KOH}</math> (2 to 3 grams dissolved in 10 cc. of water), filter and wash.</p>	<p><b>Filtrate.</b>—Contains the <math>(\text{NH}_4)_2\text{S}</math> group          a. Test for Phosphates. If found present consult notes on this group in Part II.          b. Make a test for the group, by making a small portion ammoniacal, and passing in <math>\text{H}_2\text{S}</math>, if not present. A precipitate other than sulphur indicates the presence of the metals of this group.</p>
<p><b>Precipitate.</b>—Copper group.          Analyze by procedure outlined for the insoluble <math>\text{H}_2\text{S}</math> subgroup.</p>	<p><b>Filtrate.</b>—Arsenic group in solution. Acidify, filter and analyze precipitate by the procedure for the soluble <math>\text{H}_2\text{S}</math> subgroup.          c. If a test is made for magnesium, analyze the filtrate by procedures for the alkalies.</p>

The principal non-ferrous alloys come under the following classifications

## FUSIBLE METALS

## WHITE METALS, SOLDERS, BABBITTS, ANTIFRICTION

Alloy	Composition					
	Lead	Tin	Antimony	Copper	Zinc	Other Constituents
Ordinary Bearings		96		4		
Kaysersium		92.98	5.44	1.58		
Brittania Metal		90.1	6.3	3.1	0.5	
Babbitt Metal		88.9	7.4	3.7		
Berlin Railroads		83	11	6		
Ashberry		79	15	3.0	2.0	Ni, 1.0
Minorfer		66	20	4.0	9.0	Fe, 1.0
Stereotype Metal	20.0	30.0				Bi, 50.0
Pewter		20	80			
Railroad Bearings	60.0	20	20			
Type Metal	70.0	10	18	2.0		
Magnolia Metal	80.0	4.75	15.0	Trace		Bi, .25
Tempered Lead	98.5	.08	.11			Na, 1.31
White Metal	82.0		12.0	6.0		
Solder	75.0	25.0				
Solder	50.0	50.0				
Steam Boiler Plug	48.4				38.8	Bi, 12.8
Sir Isaac Newton's Alloy	30.0	20.0				Bi, 50.0
Rose's Alloy	28.1	21.9				Bi, 50.0
Wood's Alloy	25.0	12.5				Bi, 50.0
Expanding Alloy	66.7		25.0			Cd, 12.5 Bi, 8.3

## BRONZES—PLAIN AND SPECIAL

Alloy	Composition				Remarks
	Copper	Tin	Zinc	Other Constituents	
Phono Electric Metal	98.55	1.40		Si, .05	Telephone Wire
Phono Electric Metal	95	5			
Silicon Bronze	97.00	1.45	1.50	Si, .05	
Bronze	92	8			
Phos. Bronze	90	9.8		P, .05	
U. S. Gun Metal (1875)	90	10			Medals, Whistles
Gun Metal	90	8	2		
Statuary Bronze	90	6	3	Pb, 1.0	
Arsenic Bronze	89	10		As, 1.0	Antifriction
Admiralty Bronze	88	10	2		
British Navy Bronze	87	8	5		
	87	7		Pb, 3.0	Carbureters
Locomotive Bearings	84	14			
Large Bells	85	15			
Needle Metal	84.96	7.96	5.31	Pb, 1.77	
Gun Metal	84	14	2		Valves, Screw
Japanese Bronze	83.0	5.0	2.0	Pb, 10.0	
Gun Metal	82	16	2		Bearings
Bell Metal	80	18	2		
Small Bells	80				
Ajax	77	11.5		Pb, 11.5	Bearings
Speculum Metal	70.00	30.00	Trace	Fe, Trace Ni, Trace	
Ajax Plastic	65	5.0		Pb, 30.0	Bearings
Betz Alloy	74.3	11.4		Pb, 8.9 Sb, 5.4	
Acid Resisting Metal	82.00	8.0	2.00	Pb, 7.95 P, .05	



## PLAIN BRASSES

Alloy	Composition		Remarks
	Copper	Zinc	
Tombac .....	99.15	.85	Tombac
Tombac .....	97.8	2.2	
Ctge. Gilding .....	95	5	Ctge. Gilding
Tombac .....	91.0	9	
French Oreide (Gilding) .....	90	10	
Dutch Gold .....	84.5	15.5	Imitation Gold
Bronze Powder .....	84	16	
Pinchbeck .....	83.3	16.7	
Mannheim Gold .....	80	20	4 and 1 Low Brass
3 and 1 Ctge. Brass .....	75	25	
Ctge. Brass .....	70	30	
2 and 1 Ctge. Brass .....	67	33	
Common Brass Wire ..	66.6	33.4	
Masonic Gold .....	65	35	
Common High .....	64.5	35.5	
Muntz Metal ..	60.7	40	
Bath Metal ..	55	45	
Brazing Solder ..	50	50	
Strong Brass Solder ..	33.34	66.66	

## LEADED BRASS

Alloy	Composition		
	Copper	Lead	Zinc
Leaded Orcide Wire ..	88	1.0	11
Watch Brass .....	74	1.25	24.75
Swivel Connection Wire ..	69.5	1.00	29.5
Sign Brass .....	66	.5	33.5
Drill Rod .....	63.5	3	33.5
Engravers Brass ..	63.5	2	34.5
Common Leaded Wire ..	63	2	35
Clock Brass .....	61.5	1	37.5

# ANALYSIS OF ALLOYS

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## TIN BRASS AND SPECIAL BRASS

Alloy	Composition			Other Constituents
	Copper	Tin	Zinc	
Name Plates.....	86	3.0	9	Pb, 2.0
Trolley Fittings.....	85	3.0	9	Pb, 3.0
Condenser Brass.....	70	1	29	
Tobin Bronze.....	61.00	1.00	37.50	Fe, .15 Pb, .35
Naval Brass Rod.....	61.00	1.00	38.00	
Manganese Bronze.....	57.20	1.18	40.15	Fe, 1.33 Mn, .02 Al, .10 Pb, .02
Rich's Metal.....	60.0		38.2	Fe, 1.8
Delta Metal.....	55.94		41.61	Pb, .72 Fe, .87 Mn, .84 P, .02

## CUPRO NICKEL AND NICKEL SILVERS

Alloy	Copper	Nickel	Zinc	Lead	Iron	Other Constituents
5% Nickel Silver.....	63.0	5.0	32.0			
10% Nickel Silver.....	60	10.0	30			
10% Cupro Nickel.....	90	10.0				
Swiss Watch Nickel.....	58.0	14	25.25	1.50	1.25	
15% Nickel Silver.....	63	15	22			
15% Watch Nickel.....	56	15	27.75	1.25		
15% Cupro Nickel.....	85	15				
Hardware Metal.....	50	15	34.90			Al, .10
Victor Metal.....	49.94	15.40	34.27		.28	Al, .11
Sterling.....	69.00	18.00	13.00			
Special Spoon Stock.....	61.5	18	20.5			
20% Nickel Silver.....	61.5	11	18.5			
20% Cupro Nickel.....	80	20				
U. S. Nickel Coins.....	75	25				
Argentian.....	52.0	26.0	22.0			

## Analysis of Type Metal

**Alloy of Copper, Lead, Antimony, Tin, with Small Amounts of Iron and Arsenic**

**Solution of the Alloy.** To 1 gram of the alloy, which has been cut into small shavings with a clean knife, or sampled by means of a clean hack-saw producing fine "sawings," are added 15 cc. concentrated hydrochloric acid. The solution

is gently warmed on the water bath and a drop or two of concentrated nitric acid is added occasionally until solution is effected. All of the metals will be converted into chlorides which will remain in solution with the possible exception of lead chloride. An excess of nitric acid is to be avoided, as it tends to form insoluble metastannic acid, which can be readily distinguished from the crystalline lead chloride. If metastannic acid forms, the operation must be repeated, using less nitric acid or adding it less frequently. After a few trials the correct method of adding the nitric acid is soon acquired.

**Lead.** The solution is allowed to cool and then stand at least one-half hour or better overnight to allow the lead chloride to crystallize out. Ten times the volume of absolute alcohol is then added in several portions. After standing for about half an hour, the lead chloride is filtered off on a Gooch crucible, washed with a mixture of 4 parts of 95% alcohol and 1 part of concentrated hydrochloric acid, and finally with pure alcohol. It is dried for three hours at  $150^{\circ}$  and weighed. The great advantage of this method of separating the lead is that the very troublesome treatment of the sulphides of the metals present with sodium or potassium sulphide is avoided. The *most difficult part* of the operation is the solution of the alloy.

**Copper and Iron.** The filtrate from the lead chloride is heated until the alcohol is expelled. Two grams of tartaric acid and an excess of ammonia are added and the solution warmed until the precipitate dissolves. By the addition of 5 cc. of saturated hydrogen-sulphide water, the copper and the small amount of lead still unprecipitated as well as a trace of iron which may be present may be precipitated without bringing down any of the tin and antimony. The solution is warmed and when the dark-colored precipitate has settled, 1 cc. of the hydrogen-sulphide water is added to the clear supernatant liquid. If no further precipitate is produced, the solution is filtered and the precipitate washed with water containing hydrogen sulphide.

The precipitate is dissolved in a little warm dilute nitric acid and the lead separated as sulphate, the nitric acid being expelled by evaporation after the addition of sulphuric acid. The copper is precipitated from the filtrate as sulphide and if small in amount may be ignited and weighed as oxide. If considerable copper is present it must be weighed as sulphide or without precipitation as sulphide may be separated electrolytically from the iron. One or 2 cc. concentrated nitric acid are added and a current of one-half ampere passed until all the copper is precipitated. The iron may then be precipitated with ammonia and weighed as oxide.

**Separation of Antimony and Tin.** The solution of antimony and tin is acidified with hydrochloric acid, hydrogen sulphide passed, and the precipitate filtered off and washed two or three times. A hole is made in the point of the filter-paper by means of a glass rod and the bulk of the precipitate washed into a beaker with a little water. Warm dilute hydrochloric acid is poured over the paper to dissolve the portion of the precipitate still adhering to the paper. The precipitate in the beaker is dissolved by warming and adding concentrated hydrochloric acid. The hydrogen sulphide is decomposed by the addition of a crystal of potassium chlorate and warming. Some pure metallic iron is added and the solution heated on the water bath for about one-half hour or until the iron is nearly dissolved. The precipitated antimony is filtered off on a Gooch crucible, a little iron having been sprinkled on the asbestos. The precipitate is washed with boiled water to which considerable hydrochloric acid has been added.

The antimony is dissolved in hydrochloric acid to which a little potassium chlorate has been added. The solution is warmed to expel chlorine and, after the addition of tartaric acid and water, hydrogen sulphide is passed. The antimony sulphide is filtered off and washed with water containing a little hydrogen sulphide. The moist precipitate is rinsed into a capacious porcelain crucible with water. The small portion still adhering to the paper is dissolved in a little warm ammonium sulphide and the solution allowed to flow into the crucible. The solution is evaporated on the water bath after the addition of a few cc. of concentrated nitric acid. If sulphur separates, a little liquid bromine is added when the solution has become quite concentrated. When the globule of sulphur has disappeared, expel the excess of nitric acid by heating on the hot plate or with the Bunsen burner, finally heating to full redness. Cool a little, sprinkle some ammonium carbonate over the precipitate, and ignite again to completely expel sulphuric acid and weigh as antimony tetroxide,  $\text{Sb}_2\text{O}_4$ .

The antimony may also be weighed as the trisulphide,  $\text{Sb}_2\text{S}_3$ . The precipitate is filtered on a weighed Gooch crucible, and heated to  $230^\circ$  in a stream of carbon dioxide to exclude oxygen until constant.

**Tin.** To precipitate the tin in the filtrate from the antimony the excess of hydrochloric acid is neutralized with ammonia, the solution diluted somewhat, warmed, and hydrogen sulphide passed until the tin is entirely precipitated. The stannous sulphide is washed with water containing hydrogen sulphide and a few grams of ammonium sulphate. It is dried and detached from the paper which is burned. The precipitate and the ash are placed in a weighed porcelain crucible and heated very gently with free access of air until sulphur dioxide ceases to be given off. The oxidation may be assisted by the addition of a few drops of nitric acid. Finally the precipitate is strongly heated to expel sulphuric acid, which is completely removed by the addition of a little ammonium carbonate and again igniting. It is weighed as stannic oxide,  $\text{SnO}_2$ .

**Arsenic.** As only a trace of arsenic is present, a 5- or 10-gram portion of the alloy should be taken for its determination. Dissolve in hydrochloric acid and potassium chlorate and warm to expel the chlorine. Filter off the lead chloride on asbestos and wash a few times with dilute hydrochloric acid. Add one-third the volume of concentrated hydrochloric acid and pass hydrogen sulphide. Filter off the precipitate consisting of the sulphides of copper and arsenic on asbestos, wash with hot water containing hydrogen sulphide and a little hydrochloric acid. Dissolve the arsenic sulphide by washing the precipitate with a little warm dilute ammonia. Evaporate the solution nearly to dryness in a porcelain dish. Oxidize the arsenic by warming with concentrated nitric acid, dilute the solution somewhat, neutralize with filtered ammonia, and add magnesia mixture. After standing twenty-four hours filter, wash, ignite, and weigh as magnesium pyroarsenate according to the directions given in chapter on Arsenic.

### Analysis of Soft Solder

#### **Alloy of Lead and Tin, Generally Containing Small Amounts of Arsenic, Antimony, Iron, and Zinc**

**Solution of the Alloy.** One gram of the alloy is weighed out and transferred to a beaker of about 500-cc. capacity. Ten cc. of concentrated nitric acid and 5 cc. of water are added. The beaker is covered with a watch-crystal and heated

on the water bath until the alloy is completely decomposed and the nitrous fumes are entirely expelled. One hundred cc. of water are added and the solution boiled for five minutes and allowed to settle for one hour. The stannic oxide is filtered off and washed with hot water. The moist precipitate may be introduced into a weighed porcelain crucible, the paper burned in the usual manner, and finally heated to redness for ten minutes.

**Tin.** When the precipitate has been brought to constant weight, it is fused with six times its weight of a mixture of equal parts of sulphur and sodium carbonate. The fused mass is dissolved in hot water and the solution filtered. The insoluble sulphides are washed with hot water and treated with a little dilute hydrochloric acid and the paper washed with water. If *copper* is present it will remain on the paper and the small amount present may be weighed as  $\text{CuO}$  after burning the paper in a porcelain crucible and igniting the precipitate. The lead is precipitated by the addition of a few drops of sulphuric acid and 25 cc. of alcohol to the solution, which should not exceed 50 cc. After standing one hour, the precipitate is filtered off on a Gooch crucible, washed with alcohol, dried on the hot plate, and weighed. The filtrate is evaporated until the alcohol is completely expelled. Any iron present is precipitated with ammonia and weighed. Hydrogen sulphide is passed through the filtrate to precipitate any zinc present, which is filtered off. The filtrate from the insoluble sulphides will contain the tin as a thiostannate and part of the *antimony* present in the alloy as a thioantimonate. The solution is boiled after the addition of caustic soda and hydrogen peroxide until it is nearly decolorized. On acidifying and passing hydrogen sulphide both metals are precipitated as sulphides. If antimony is present the metals should be separated by the method given under Analysis of Type Metal, page 1076. The weight of the impurities found, computed as oxides, is deducted from the weight of the impure stannic oxide.

**Lead.** The filtrate from the stannic oxide is transferred to a porcelain dish, 5 cc. concentrated sulphuric acid added, and evaporated until fumes of sulphuric acid are evolved. Cool the dish by floating it in cold water and add cautiously 75 cc. of water. Stir thoroughly and add 25 cc. of alcohol. Allow the solution to stand for at least one hour, filter off the lead sulphate on a weighed Gooch crucible, wash with alcohol until free from acid, dry on the hot plate, and weigh.

**Arsenic and Antimony.** The alcohol is completely expelled from the filtrate by evaporation and any arsenic present precipitated by passing hydrogen sulphide. If this precipitate is of an orange color instead of pure yellow, antimony is present. It should be filtered off and washed with water containing a little hydrochloric acid until free from iron and hydrogen sulphide. It is then washed with small portions of concentrated ammonium carbonate solution until the arsenic sulphide is entirely dissolved. The arsenic is reprecipitated by acidifying the solution with hydrochloric acid and passing hydrogen sulphide. It is filtered off on a Gooch crucible and washed with water containing hydrogen sulphide and a little hydrochloric acid. The water is removed by alcohol and the precipitate digested with carbon disulphide until sulphur is entirely removed. The arsenic sulphide is dried at  $100^\circ$  and weighed. If antimony is absent the treatment with ammonium carbonate is omitted, the precipitate being filtered off on a Gooch crucible, washed, dried, and weighed. If antimony is present it is ignited and weighed as directed in page 1076 under the Analysis of Type Metal.

**Iron.** A few drops of bromine water are added and the solution is boiled to oxidize the iron and to expel the hydrogen sulphide. The iron is then precipitated by

making the filtrate alkaline with filtered ammonia and warming for a few minutes. It is filtered off on a small paper and dissolved by adding a few drops of dilute hydrochloric acid. The paper is washed with about 75 cc. of water in small portions. The iron is reprecipitated and filtered on the same paper after moistening with a few drops of ammonia. After washing free from chlorides, the moist paper is transferred to the weighed platinum crucible and ignited.

**Zinc.** Hydrogen sulphide is passed into the combined filtrates to precipitate any zinc present, which is filtered off, washed, and weighed as sulphide after ignition with sulphur in a stream of hydrogen.

### Analysis of Rose's Metal

#### Alloy of Lead, Bismuth, and Tin, Generally Containing Small Amounts of Copper, Arsenic, Antimony, Iron and Zinc

One gram of the metal is weighed out and decomposed with nitric acid and the *stannic oxide* is weighed, according to the procedure under analysis of soft solder, page 1078.

**Lead.** To the filtrate from the stannic oxide containing the nitrates of lead and bismuth, 5 cc. concentrated sulphuric acid are added. The solution is evaporated in a porcelain dish until sulphuric-acid fumes are given off. The dish may be placed on the hot plate, sand bath, or wire gauze and the liquid heated to just below the boiling-point to avoid spattering. When the acid becomes concentrated, the heat may be somewhat increased. The hot concentrated solution is diluted by slowly pouring it with constant stirring into about 100 cc. of water and digested hot for about half an hour with occasional stirring. The lead sulphate is then filtered off on a Gooch crucible, washed with 10% sulphuric acid until the wash-water no longer gives a precipitate on making it alkaline with ammonia, adding ammonium carbonate, and warming. The sulphuric acid is then washed out with alcohol. The precipitate is dried and weighed. It is tested for a possible contamination with bismuth as follows: It is dissolved in 5 to 10 cc. of warm concentrated hydrochloric acid and 50 cc. of absolute alcohol are added to the solution. After standing for a few moments, the solution, containing the bismuth as chloride, is filtered off. By nearly neutralizing with ammonia, and largely diluting with water, the bismuth is precipitated as oxychloride and may be washed with water containing a few drops of hydrochloric acid, dried, and weighed.

**Bismuth.** In the filtrate from the lead sulphate, the bismuth is precipitated by just neutralizing with filtered ammonia, adding a few drops of ammonium carbonate and warming the solution gently for about fifteen minutes. The precipitate is filtered off and washed a few times with water. To free the precipitate from a small amount of basic sulphate it is dissolved in a small amount of dilute nitric acid and reprecipitated. The precipitate is washed with water containing a little ammonium nitrate and dried. It is removed from the paper as completely as possible and placed on a watch-crystal. The paper is replaced in the funnel, moistened with a few drops of dilute nitric acid, and washed with small amounts of warm water. The wash-water is evaporated to dryness in a fairly large weighed porcelain crucible, and the residue ignited until the nitric acid is completely expelled. The main portion of the precipitate is now added, heated with the Bunsen burner and weighed as  $\text{Bi}_2\text{O}_3$ .

**Copper.** If copper is present in the alloy, it will be contained in the two

filtrates from the bismuth precipitate. Combine these filtrates, acidify with hydrochloric acid, and concentrate to a convenient bulk. Pass hydrogen sulphide through the warm solution, filter, and wash with water containing hydrogen sulphide. Even if copper is absent, a small black precipitate of bismuth sulphide will be obtained at this point because of the slight solubility of the bismuth hydroxide or carbonate. The precipitate may be tested for bismuth by treating with a little dilute hydrochloric acid and diluting the filtrate. A white precipitate indicates bismuth. The copper sulphide, being insoluble in dilute hydrochloric acid, remains on the paper and may be ignited together with the paper and weighed as oxide. If *arsenic, antimony, iron* or *zinc* are present they are separated and determined by the methods given under pages 1076, 1077 and 1085.

### Analysis of Wood's Metal

#### **Alloy of Lead, Bismuth, Tin, and Cadmium, Generally Containing Small Amounts of Copper, Arsenic, Antimony, Iron and Zinc**

One gram of the metal is weighed, dissolved in nitric acid, and the *stannic oxide* weighed and purified. The filtrate from the tin is evaporated to dryness on a water bath. The nitrates are converted into chlorides by evaporating twice on the water bath to a small bulk after the addition of 20 cc. of concentrated hydrochloric acid.

**Lead.** After cooling, 25 cc. absolute alcohol are added. The mixture is stirred and after standing some time the chloride of lead is filtered off on a Gooch crucible, and washed with an ice-cold mixture of 4 parts of 95% alcohol and 1 part of concentrated hydrochloric acid. It is dried on the hot plate or at 150° for three hours and weighed.

**Bismuth.** The filtrate is diluted with about one-half liter of water and nearly neutralized with ammonia (about 40 cc. of dilute ammonia will be required). After standing twenty-four hours the bismuth oxychloride is filtered off on a Gooch crucible, washed with water containing a few drops of dilute hydrochloric acid, dried at 110°, and weighed as  $\text{BiOCl}$ .

The bismuth may also be precipitated as bismuth hydroxide by volatilizing most of the alcohol, neutralizing with ammonia and warming gently. If *iron* is present this precipitate will be reddish. In that case it is best to dissolve it in hydrochloric acid and precipitate the bismuth as oxychloride. The bismuth hydroxide is ignited and weighed as oxide,  $\text{Bi}_2\text{O}_3$ .

**Cadmium.** The filtrate from the bismuth oxychloride is evaporated to a bulk of 200 or 300 cc. If the bismuth has been precipitated by means of ammonia, the filtrate is first acidified with hydrochloric acid and evaporated to a moderate bulk. The solution is saturated with hydrogen sulphide and the precipitate filtered off and washed with water containing hydrogen sulphide. If the cadmium sulphide is dark colored or black, traces of lead or bismuth sulphides may be present because of incomplete separations, or copper may have been present in the alloy. Any arsenic which may have been in the alloy or a trace of tin or antimony will also be present in this precipitate.

**Arsenic, Antimony, and Tin.** It should be tested for these three elements by pouring over it a few drops of warm potassium or sodium sulphide and washing two or three times with warm water, being careful to stir up the precipitate with the stream of water from the wash-bottle. A precipitate formed on acidifying the

filtrate indicates the presence of arsenic, antimony, or tin. If the characteristic orange color of antimony is absent, the supernatant liquid should be decanted and the precipitate warmed with a little concentrated hydrochloric acid. If it dissolves completely, arsenic is absent and the tin may be reprecipitated by diluting and passing hydrogen sulphide. After washing, the moist precipitate with the paper may be burned and the sulphide of tin converted into oxide by ignition. If arsenic or antimony is present, it may be determined as directed in the Analysis of Type Metal, page 1076.

**Separation of Copper and Cadmium.** To dissolve out any copper which may be present with the cadmium sulphide, a few drops of potassium cyanide should be poured over the precipitate. It should be thoroughly stirred up with water and washed a few times. If a considerable amount of copper is present, the bulk of the precipitate should be transferred to a beaker by washing out the paper while still in the funnel with a stream of water. The remainder of the precipitate on the paper is dissolved by washing with a little warm dilute nitric acid. The paper is then thoroughly washed with small portions of hot water. The washings are allowed to flow into the beaker containing the main portion of the precipitate. The beaker is warmed and more nitric acid is added if necessary to dissolve the precipitate. The solution is neutralized with sodium carbonate and a slight excess of potassium cyanide added. A small white precipitate at this point may be lead or bismuth carbonates, which should be filtered off and determined. On passing hydrogen sulphide through the filtrate, the cadmium is precipitated as sulphide and may be filtered off on a Gooch crucible and washed with water containing a little hydrogen sulphide. It is finally washed with pure water and the free sulphur extracted by washing with alcohol and then with carbon disulphide. The precipitate is dried at  $100^{\circ}$  and weighed.

**Copper.** The filtrate from the cadmium sulphide contains the copper and is acidified<sup>1</sup> with sulphuric acid and a little nitric acid and evaporated to fumes. The residue is dissolved in water, filtered if necessary, and the copper precipitated as sulphide. If it is small in amount it may be ignited and weighed as oxide. If considerable copper is present, it must be ignited with sulphur in a stream of hydrogen and weighed as cuprous sulphide,  $\text{Cu}_2\text{S}$ . When much copper is present, it is better to determine it electrolytically.

**Separation of Iron and Zinc.** The filtrate from the first precipitation with hydrogen sulphide contains any zinc or iron which may have been present. These metals may be separated in the following manner:

The solution is boiled to expel hydrogen sulphide, neutralized with ammonia, and acidified with acetic acid. Hydrogen sulphide is passed for some time and the solution allowed to stand for several hours. The clear liquid is carefully decanted through a filter paper, and after replacing the beaker containing the clear filtrate with another beaker, the sulphide of zinc is brought on the paper and washed with water containing ammonium acetate and acetic acid. The precipitate is dissolved in a little dilute nitric acid and the paper washed with hot water. The solution of the zinc is evaporated to dryness in a weighed porcelain crucible, ignited finally over the blast-lamp to decompose any zinc sulphate which may have been formed, and weighed as oxide. The filtrate is boiled to expel the hydrogen sulphide. A little nitric acid is then added to oxidize the iron, which is precipitated with

<sup>1</sup> This should be done under a hood with good draught to avoid any possibility of inhaling the very poisonous hydrocyanic-acid fumes.



ammonia and weighed as oxide. A very convenient method of oxidizing the iron and removing the hydrogen sulphide is by the use of bromine water. The bromine should be added until the solution is colored, indicating complete oxidation of the iron and the presence of an excess of bromine. If a solution of bromine in concentrated hydrochloric acid is used a few drops will suffice and the solution will not be diluted to any extent. If manganese is to be removed together with iron, the presence of an excess of bromine is advantageous; otherwise it must be boiled out. As the bromine oxidizes hydrogen sulphide in the cold, the excess of the latter need not be boiled out.

### Analysis of Britannia Metal

#### Alloy of Tin, Antimony, and Copper, with Small Amounts of Bismuth, Lead, and Iron

**Decomposition of the Alloy by Means of Chlorine.** Alloys containing a large percentage of tin are best decomposed by a stream of chlorine. The method is applicable to alloys containing less than 15% of lead and copper.

A hard-glass combustion-tube 70 cm. long is taken and one end drawn out, making a small tube 20 cm. long, which is bent at right angles. This small tube is connected by means of a cork stopper with a Peligot tube the bulbs of which are nearly filled with dilute hydrochloric acid (1 : 3) containing about 1 gram of tartaric acid. A second Peligot tube is connected with the first and contains a solution of caustic soda (1 : 3). The chlorine is evolved in a 2-liter flask containing pieces of pyrolusite, over which concentrated hydrochloric acid is poured. The flask is heated on a water bath. The chlorine is passed through a wash-bottle containing water and then through two wash-bottles containing sulphuric acid. It is then passed into the combustion-tube, connection being made by means of a cork stopper. Wherever rubber is used for making connections, it must be well coated with paraffin. This is also advisable for the cork stoppers. The chlorine is not allowed to pass into the combustion-tube until all of the air has been displaced from the flask and the wash-bottles. All escaping chlorine should be absorbed in caustic-soda solution.

One gram of the alloy in *fine* turnings is weighed out and placed in a porcelain boat which is placed in the middle of the combustion-tube. The chlorine is first allowed to act on the alloy in the cold. When no further action is observed, the part of the tube in which the boat is situated is heated gently with the Bunsen burner, and then more strongly until the contents of the boat fuse. The *chlorides* of *mercury, bismuth, arsenic, antimony, and tin volatilize* and are driven out of the tube by heating it gently from the boat to the end which is drawn out. These chlorides are absorbed in the hydrochloric acid contained in the first Peligot tube, while the excess of chlorine is absorbed in the caustic-soda solution contained in the second Peligot tube.

The chlorine in the apparatus is then displaced by means of a stream of dry air or carbon dioxide, the chlorine generator having been removed. The apparatus is disconnected, the boat containing the *chlorides* of *copper, lead, and iron* is placed in a porcelain dish, and the tube washed out with hot water which is allowed to flow into the dish containing the boat. Hydrochloric acid is added and the dish warmed until the contents of the boat are dissolved. The latter is removed and washed.

**Lead, Copper, and Iron.** The lead is precipitated by evaporation with sulphuric acid and diluting and is filtered off and weighed as sulphate. The copper is precipitated by means of hydrogen sulphide and weighed as sulphide or determined electrolytically from a nitric acid solution. The iron is precipitated by means of ammonia and weighed as oxide.

The contents of the first Peligot tube are poured into a beaker and the Peligot tube well washed out with water to which hydrochloric acid is added if necessary. The solution is warmed and hydrogen sulphide passed until precipitation is complete. The filtrate should be heated to boiling, strong hydrochloric acid added, and hydrogen sulphide passed again to precipitate the arsenic.

**Bismuth.** If the sulphide precipitate is dark colored, bismuth is present. The precipitate is washed into a beaker, ammonium sulphide added, and the solution warmed. The solution is filtered through the same paper and the precipitate washed with warm water containing a little ammonium sulphide. The bismuth sulphide is dissolved in a little warm dilute nitric acid and the paper washed. The bismuth is precipitated with ammonia and ammonium carbonate, ignited, and weighed as oxide,  $\text{Bi}_2\text{O}_3$ .

**Separation of Tin from Arsenic and Antimony.** The ammonium-sulphide solution of arsenic, antimony, and tin is poured with vigorous stirring into a hot solution of 25 grams of oxalic acid in 200 cc. of water. The solution is heated to boiling and hydrogen sulphide passed for about fifteen minutes. The precipitate is filtered off immediately and washed with hot water containing hydrogen sulphide. It is dissolved in ammonium sulphide and the treatment with hot oxalic acid and hydrogen sulphide repeated.

**Tin.** The oxalic-acid solution of tin is evaporated down, with the addition of 5 cc. concentrated sulphuric acid, to fumes. The solution is cooled, cautiously diluted with water, and hydrogen sulphide passed to insure complete precipitation of the tin. Wash the precipitate with water containing ammonium acetate and a little acetic acid, dry, ignite, and weigh as stannic oxide,  $\text{SnO}_2$ .

**Arsenic and Antimony.** The precipitate of arsenic and antimony sulphides is treated with a little concentrated ammonium-carbonate solution and washed to remove arsenic. The antimony is then weighed as oxide according to the directions given under the Analysis of Type Metal, page 1076. The arsenic is determined according to the directions given in the same section.

### Analysis of Brass or Bronze

**Alloy of Lead, Copper, Tin, and Zinc, with Small Amounts of Arsenic, Antimony, Cadmium, and Iron.**

**Solution of the Alloy.** Weigh out 1 gram of the alloy and place in a 300-cc. beaker, add 10 cc. concentrated nitric acid and 5 cc. water. Cover the beaker with a watch-crystal and place in a dish of cold water. After one-half hour place the beaker on the water bath and evaporate the solution to dryness. One hundred cc. of boiling water and a few drops of nitric acid are added and the solution boiled for five minutes.

**Tin.** The stannic oxide is filtered off and washed with hot water. The moist precipitate is introduced into a weighed porcelain crucible and the paper burned in the usual manner. If the amount of tin is small (less than 1%) it is weighed at this point, otherwise it is fused with six times its weight of a mixture of equal

parts of sulphur and sodium carbonate. The fused mass is dissolved in hot water and the solution filtered. The *copper, lead, and iron* which were carried down with the stannic oxide will remain on the paper as sulphides, while the filtrate will contain all of the tin and any *arsenic or antimony* which may have been present. The insoluble sulphides are dissolved in a little nitric acid, the paper washed, and the solution added to the filtrate from the stannic oxide.

If arsenic and antimony are absent, the tin may be precipitated out of the sodium sulphide solution and weighed. The excess of sulphur should first be removed from the solution by heating to boiling after the addition of caustic soda and then adding hydrogen peroxide in small quantities until the solution is nearly decolorized. It is then acidified with hydrochloric acid while stirring constantly, heated, and hydrogen sulphide passed. The stannic sulphide is washed with hot water containing ammonium acetate and a little acetic acid. It is ignited and weighed as stannic oxide in the usual manner.

**Arsenic and Antimony.** If arsenic is present in the alloy, a small amount of this element will be present in the sodium sulphide solution of the tin and will be precipitated with the stannic sulphide. It may be removed by treating the precipitate with a little concentrated solution of ammonium carbonate and washing. The solution of arsenic should be added to the nitric acid solution of the alloy.

If antimony is also present in the alloy, the sulphides of arsenic, antimony, and tin must be separated by one of the methods given under Analysis of Type Metal, page 1076.

**Distillation Method for Determination of Arsenic in Brass.** If arsenic is present in amounts less than 0.10 per cent, 100 gram sample is taken and dissolved in 400 cc.  $\text{HNO}_3$  (sp. gr. 1.42). The fumes are expelled by boiling and the solution diluted with water to 500 cc.  $\text{NH}_4\text{OH}$  is added until a slight precipitate of copper hydroxide forms; about 5 grams of  $\text{Fe}_2(\text{SO}_4)_3$  and just enough  $\text{NH}_4\text{OH}$  to cause precipitation are added, the solution diluted to 1000 cc. and boiled. Then again diluted and the precipitate allowed to settle several hours. The clear solution is decanted off and the  $\text{Fe}(\text{OH})_3$  containing all the arsenic and antimony is washed, dissolved in hot  $\text{HCl}$ , about 2 cc. of hypophosphorous acid added and the arsenic distilled according to the procedure described on page 34, omitting the addition of  $\text{Cu}_2\text{Cl}_2$ . Arsenic may now be determined in the distillate either as  $\text{As}_2\text{S}_3$  or by titration with iodine (see pages 36 and 39).

If antimony is desired in the analysis it may be obtained in the residue remaining in the flask (see page 23).

Mr. Price recommends treating the sulphides with  $\text{CS}_2$  to remove any free sulphur that may be present. ("Technical Analysis of Brass," pages 225-227.)

If arsenic is present in amounts over 0.10 per cent, 5 grams of the alloy are dissolved in 20 cc.  $\text{HNO}_3$  (sp. gr. 1.42) and then evaporated with 15 cc.  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to fumes. Concentrated  $\text{HCl}$  may now be added, together with 2 cc. 30% hypophosphorous acid and the arsenic distilled and determined as outlined above.

**Lead.** To filtrate from the stannic oxide, 5 cc. concentrated sulphuric acid are added and the solution evaporated in a porcelain dish until the nitric acid is entirely expelled and white fumes of sulphuric acid are given off. The solution is cooled by floating the dish on cold water and diluted with 75 cc. of water. Lead is now determined as  $\text{PbSO}_4$ . See page 274.

**Determination of Cadmium in Brass.** Ten grams of drillings are dissolved in  $\text{HNO}_3$  (sp.gr. 1.42), 50 cc.  $\text{H}_2\text{SO}_4$  (sp.gr. 1.84) added and the mixture evaporated to fumes. The cooled mixture is diluted to 200 cc. with water and boiled. The precipitate is allowed to settle (several hours) and filtered off. The solution containing the cadmium is treated, boiling hot, with  $\text{H}_2\text{S}$  for thirty minutes, the precipitated sulphides filtered off and washed with hot water. The precipitate is dissolved in 400 cc. of 10 per cent  $\text{H}_2\text{SO}_4$ .

After boiling, the hot solution is filtered, cooled and treated with  $\text{H}_2\text{S}$  for ten minutes.  $\text{NH}_4\text{OH}$  is added cautiously until  $\text{ZnS}$  begins to precipitate. The solution is again treated with  $\text{H}_2\text{S}$  for about five minutes, whereupon  $\text{CdS}$  is completely precipitated. The sulphide is purified by redissolving in 100 cc. of 10 per cent  $\text{H}_2\text{SO}_4$ , applying heat. The solution is filtered, diluted to 300 cc. and again treated with  $\text{H}_2\text{S}$ . Ammonia is added drop by drop until the cadmium sulphide is completely precipitated. The treatment is repeated to remove traces of impurities and the  $\text{CdS}$  then weighed in a tared Gooch crucible after drying for two hours at  $110^\circ \text{C}$ .

Weight  $\text{CdS} \times 0.778$  = weight of cadmium.

**NOTE.**—Details of the procedure for determining minute amounts of cadmium (less than 0.01 per cent) may be found in Price and Mead, "Technical Analysis of Brass," 2d Ed., page 232, John Wiley & Sons, Publishers.

The copper is best determined electrolytically. The filtrate from the lead sulphate is heated on the hot plate until most of the alcohol is expelled. Two cc. concentrated nitric acid are added and the warm solution (about  $60^\circ$ ) electrolyzed with a current of  $\frac{1}{2}$  to 1 ampere for about six hours. If a gauze electrode is used or one of the electrodes is rotated the time required is very much reduced.

Hydrogen sulphide is passed through the acid filtrate from the copper to precipitate traces of *arsenic, antimony*, or unseparated *tin* which may be present. If more than traces are found, the metals must be separated and determined by the methods given in the preceding methods. When the amount of copper is large, as is generally the case, it is advisable to divide the solution into two portions for the electrolysis, as about 300 milligrams of copper is generally sufficient for a good determination. The solution may be divided by weighing it and then pouring out about half of it and again weighing or the solution may be diluted to a known volume as 250 or 500 cc. and a portion measured out. The copper may be determined in each portion and the filtrates combined for the zinc determination. For the duplicate zinc determination the copper may be precipitated as sulphide, which is filtered off, well washed, and discarded.

**Iron.** The filtrate from the copper is boiled to expel hydrogen sulphide and a little nitric acid added to oxidize the iron, which is precipitated with ammonia and weighed as oxide. If more than a small amount of iron is present, the precipitate must be redissolved and reprecipitated to separate it completely from the zinc.

**Zinc.**<sup>1</sup> The filtrate from the iron is evaporated to small bulk and the zinc precipitated and weighed as pyrophosphate. The zinc may also be precipitated and weighed as sulphide.

## Analysis of German Silver

**Alloy of Copper, Zinc, and Nickel, with Small Amounts of Lead, Iron, and Tin**

One gram of the alloy is weighed out and dissolved in nitric acid as directed in the preceding exercise. The *tin*, *lead*, and *copper* are determined as directed in the same exercise.

Hydrogen sulphide is passed through the acid filtrate from the copper to precipitate traces of *arsenic*, *antimony*, *tin*, or unseparated *copper* which may be present. If more than traces are found, the metals must be separated and determined by the methods given under Analysis of Type Metal, page 1076.

**Zinc.**<sup>1</sup> The filtrate is boiled until the hydrogen sulphide is expelled and the solution concentrated to a small bulk and the acid nearly neutralized with caustic soda. Five to 10 grams of caustic soda are dissolved in about 50 cc. of water and the solution of zinc and nickel added slowly with constant stirring. The solution is diluted with an equal bulk of water and the precipitate filtered off and washed. The zinc in the filtrate is precipitated with hydrogen sulphide, filtered off, and washed free from alkali. The zinc sulphide is dried and detached from the paper as completely as possible.

The portion still adhering to the paper is dissolved in nitric acid and the solution evaporated to dryness in a porcelain crucible. The remainder of the precipitate is added and the whole ignited with sulphur in a stream of hydrogen. If the precipitate is small it need not be dried, but is immediately dissolved in nitric acid and after evaporation converted into sulphide. The sulphide is tested for alkali by digestion with hot water. If alkali is found, it must be completely extracted and the sulphide again weighed after ignition with sulphur in hydrogen. The precipitate is then dissolved in nitric acid and the solution evaporated to dryness. The zinc nitrate is dissolved in water and the silica filtered off, washed, ignited, and weighed. The zinc sulphide may also be dissolved in hydrochloric acid, the zinc precipitated as zinc ammonium phosphate and weighed as pyrophosphate.

**Iron and Nickel.** If iron is absent, the nickel hydroxide may be washed and after transferring the precipitate to a weighed porcelain crucible and burning the paper it may be reduced to metallic nickel by heating in a stream of hydrogen and weighed. If iron is present, the precipitate is dissolved in hydrochloric acid and the iron precipitated with ammonia. Unless a very small amount is present it must be redissolved and reprecipitated, and, after washing, is ignited and weighed as oxide. The nickel is then reprecipitated as hydroxide by means of an excess of caustic soda, reduced in a stream of hydrogen and weighed as the metal.

<sup>1</sup> In modern practice zinc is preferably determined by weighing as oxide or by titrating with ferro-cyanide according to procedures given in the chapter on Zinc.

Note by the Editor.

**Analysis of Manganese-Phosphorus-Bronze**

**Alloy of Copper, Lead, Tin, Zinc, Manganese, Phosphorus (less than 1%),  
Traces of Iron**

**Solution.** One gram of the alloy is weighed out and dissolved in nitric acid. Nearly all of the phosphorus remains with the stannic oxide as a phosphate. After fusing the impure precipitate and separating the impurities, and precipitating the tin as sulphide, the solution containing only the phosphorus as phosphoric acid is discarded, as this element is determined in a separate portion of the alloy.

**Lead, Copper, and Zinc** are determined as given under Analysis of Brass and Bronze, page 668. The phosphoric acid which did not remain with the stannic oxide will be present in the alkaline solution of the zinc. This element should therefore be precipitated and weighed as pyrophosphate.

**Iron.** In order to separate manganese and iron from zinc, bromine or hydrogen peroxide is added to the filtrate from the copper. The solution is boiled and excess of ammonium added to redissolve any zinc phosphate which may be precipitated. The precipitate consisting of ferric hydroxide and manganese dioxide is filtered off and washed. It is dissolved in a little hydrochloric acid and the paper well washed. The solution is boiled until the chlorine is completely expelled, then neutralized with ammonia, warmed, and the trace of iron filtered off immediately. Unless the precipitate is very small it is redissolved in hydrochloric acid and again precipitated with ammonia and quickly filtered off and washed. It is ignited and weighed as oxide.

**Manganese.** The combined filtrates from the iron contain all of the manganese unless the amount of iron present is considerable. The solution should be evaporated to dryness in a porcelain dish and the ammonium chloride volatilized by gently heating with the Bunsen burner. The residue is dissolved in a few cc. of water and a few drops of hydrochloric acid and the manganese precipitated and weighed as sulphide.

**Volumetric Determination of Iron and Manganese.** If considerable iron is present, the method of separation given is not applicable. In this case the simplest methods of determining the two metals are volumetric. The ammonium precipitate should be dissolved in sulphuric acid with the addition of a little hydrogen peroxide, the excess of which may be expelled by boiling. The solution must be made up to a definite volume and divided into two equal portions. For this purpose a 100-cc. flask should be used which has been calibrated with a 50-cc. pipette by emptying the pipette twice into the dry flask and making a mark on the stem. The solution of iron and manganese is evaporated to small bulk, transferred to the flask, made up to the mark and thoroughly mixed. Fifty cc. are withdrawn with the dry pipette. The solution adhering to the walls of the pipette is rinsed out with distilled water and added to the portion remaining in the flask. One of these portions is reduced with zinc and the iron titrated with standard permanganate. (See p. 253.) The other portion is shaken up with zinc oxide until the free acid is neutralized. One gram of zinc sulphate and a drop or two of dilute nitric acid are added and the solution diluted to several hundred cubic centimeters. The manganese is titrated with standard potassium permanganate according to Volhard. (See page 304.)

**Phosphorus.** For the determination of phosphorus a 5-gram portion of the alloy is taken, as the percentage of this element is usually small (seldom more than

0.2%). The material is placed in a 200-cc. beaker and 20 to 30 cc. concentrated nitric acid added. The beaker is covered with a watch-crystal and after the first violent action of the acid has ceased it is placed on the water bath and heated until the alloy is completely decomposed and the residue is pure white. All of the phosphoric acid will remain with the tin provided a sufficient amount of the latter is present in the alloy. From six to eight times as much tin as  $P_2O_5$  must be present. Unless at least 5% of tin has been found, a preliminary test should be made by dissolving about a gram of the alloy in concentrated nitric acid, filtering, and testing the filtrate for phosphoric acid with molybdate mixture. If phosphoric acid is found in the filtrate, metallic tin must be added before dissolving the alloy in nitric acid. From  $\frac{1}{2}$  to 1 gram will usually be found sufficient.

The nitric acid solution of the alloy is diluted and the stannic oxide containing the phosphoric acid is filtered off and washed a few times. After drying, the precipitate is transferred to a porcelain crucible, the paper is burned, and the ash added. After adding three times its weight of potassium cyanide, cover the crucible and fuse for a few minutes at a red heat. The stannic oxide is reduced to metallic tin and the phosphoric acid forms potassium phosphate. After cooling, extract the fused mass with hot water, filter, and wash the paper with hot water.

Expel the hydrocyanic and cyanic acids by boiling with concentrated hydrochloric acid. *This operation must be conducted under a hood with good draught.* Evaporate to dryness to dehydrate the silicic acid which has been dissolved from the porcelain by the action of the potassium cyanide. Dissolve the dry residue in a little hydrochloric acid and pass hydrogen sulphide to precipitate a small amount of tin and copper which is present. Filter, wash the precipitate, and destroy the hydrogen sulphide in the filtrate by adding bromine water and boiling. If the volume of the solution exceeds 50 cc., concentrate by boiling. Cool and precipitate the phosphoric acid by adding about  $\frac{1}{2}$  gram of crystallised magnesium chloride or sulphate dissolved in a little water and then neutralizing the solution with filtered ammonia while stirring vigorously. Add a small excess of ammonia. *Assure yourself that the phosphoric acid is all precipitated by adding a little magnesia mixture to the clear supernatant liquid.* After standing several hours, filter, wash with dilute ammonia, ignite in a porcelain crucible, and weigh as magnesium pyrophosphate.

The precipitation of the metals present with hydrogen sulphide may be omitted and the separation effected by precipitating the phosphoric acid as molybdate. The dry residue should then be dissolved in nitric acid, and after filtering off the silica, the phosphoric acid is precipitated as directed in the chapter on Phosphorus.

NOTE. *See next of Acids Used in Alloy Analysis.* Concentrated HCl, sp. gr. 1.19; concentrated  $HNO_3$ , sp. gr. 1.42; concentrated  $H_2SO_4$ , sp. gr. 1.84.

### Analysis of Manganese bronze

*Standard Method, A. S. T. M.*

**General Considerations.** Methods are given for the determination of lead, using a large sample when lead is present up to about 0.2 per cent. A method is also given for the electrolytic determination of lead and copper in the same small sample when lead is present in amounts over 0.2 per cent.

In this alloy zinc is taken by difference.

#### **Alloy of Copper, Lead, Tin, Iron, Manganese and Zinc Determination of Copper by the Electrolytic Method**

**Apparatus for Electrolysis.** *Electrodes:* The electrodes recommended are of the stationary and not of the rotating type, as the stationary require less operator's time and there is less chance for erroneous results to be obtained than with the other kind. Rapid and accurate results are obtained with stationary electrodes made from platinum gauze.

*Cathodes:* Platinum cathodes may be formed either from plain or perforated sheets, or from wire gauze, and may be either open or closed cylinders. They should give a depositing surface, counting both sides, of approximately 100 sq. cm. Gauze cathodes are recommended, and are best made from gauze containing approximately 400 meshes per sq. cm. (45 meshes per linear inch). The cathode should be stiffened by doubling the gauze for about 3 mm. at the top and at the bottom of the cylinder. The cylinder should be approximately 30 mm. in diameter and 30 mm. in height. The stem should be made from 1.14 mm. or 1.29 mm. wire, flattened and welded the entire width of the gauze; the height over all should be approximately 135 mm., and the gauze should be sand blasted.

*Anodes:* Platinum anodes may be of the spiral type when used in the determination of copper by electrolysis, or in the electrolytic determination of lead when it is present in amounts not over 0.2 per cent. When used in electrolytic determination of copper and lead together in samples containing 0.2 per cent lead or over, the anodes should be of wire gauze. Spiral anodes should be made from 1.02 mm. or 1.14 mm. wire formed into a spiral of 7 turns having a height of approximately 51 mm. and a diameter of 16 mm., the length over all being approximately 145 mm. Platinum gauze used in making anodes should contain approximately 400 meshes per sq. cm. (45 meshes per linear inch). The gauze should be formed into closed cylinders approximately 12 mm. in diameter and 30 mm. in height. The cylinders should be stiffened by doubling the gauze for about 3 mm. at the top and at the bottom. The stem should be made from 1.02 mm. or 1.29 mm. wire, flattened and welded the entire width of the gauze; the height over all should be approximately 135 mm., and the gauze should be sand blasted.

**NOTE.** The original spelling adopted by the A. S. T. M. is used throughout this section on alloys. The methods appear in the form recommended, without alteration.



**Method.** In a 150 cc. beaker dissolve 1 g. of bronze in 10 cc. of  $\text{HNO}_3$ , sp. gr. 1.42. When the action has ceased, evaporate the solution to dryness, and bake thoroughly on the edge of a hot plate. Moisten thoroughly with  $\text{HNO}_3$ , sp. gr. 1.42, and after digesting for a short time dilute to 50 cc. with distilled water, heat to boiling, and allow to stand and settle for about one hour, keeping the temperature just below the boiling point. Filter on double 7 cm. papers, keeping the solution hot, and receive the filtrate in a 200 cc. electrolysis beaker. Wash with boiling hot water. Add to the filtrate 5 cc. of  $\text{H}_2\text{SO}_4$ , sp. gr. 1.84, and evaporate until copious fumes of  $\text{H}_2\text{SO}_4$  are evolved. Dilute to about 100 cc. with distilled water, add 1.5 cc. of  $\text{HNO}_3$ , sp. gr. 1.42 insert electrodes, cover with a pair of split watch-glasses and electrolyze. For each solution use a current over night of 0.5 ampere at approximately 10 volts, or else use a current of 4 amperes at approximately 10 volts continued for about  $2\frac{1}{2}$  hours. The latter case requires the use of gauze cathodes. When the solution is colorless, wash down cover glasses, electrodes, and sides of beaker, raising the level of the liquid slightly and continue the electrolysis about 15 minutes, noting whether or not copper is deposited on the newly exposed surface of the platinum. If no copper appears, transfer about 1 cc. of the colorless solution to the cavity of a porcelain test plate, and add a few drops of fresh  $\text{H}_2\text{S}$  water. If the slightest discoloration occurs continue the electrolysis, repeating the test. Remove the cathode quickly, rinse it in distilled water and then dip it in two successive baths of alcohol. Shake off the excess alcohol and ignite the remainder by bringing it to the flame of an alcohol lamp. Keep the cathode moving continually as the alcohol burns. Weigh as metallic copper.

**Accuracy:** Duplicate determinations should check within 0.10 per cent of copper.

**Notes.** In alloys of the type of manganese bronze, which carry considerable iron, it is impossible to remove the tin quantitatively as metastannic acid ( $\text{H}_2\text{SnO}_3$ ), notwithstanding the preliminary baking. Upon testing (by the addition of  $\text{H}_2\text{S}$  water), the liquid in the pits of the test plate may be colored yellow, due to the tin present, but there should be no darkening due to the presence of copper. If the cathode appears dark, as though tin had been deposited on it, dissolve the coating in 10 cc. of  $\text{HNO}_3$ , sp. gr. 1.42, filter off the tin as before, add to the filtrate 5 cc. of  $\text{H}_2\text{SO}_4$ , sp. gr. 1.84, and redeposit copper by electrolysis. It is rarely necessary thus to purify the deposited copper.

If zinc is to be determined in the alloy be careful to keep the solution quantitative when the electrodes are removed, catching all washings in the beaker containing the electrolyte.

**Determination of Lead by the Electrolytic Method****(For Samples Containing up to 0.2 Per Cent of Lead)**

**Method.** In a 250 cc. beaker dissolve 5 g. of bronze in 25 cc. of  $\text{HNO}_3$ , sp.gr. 1.42. Allow the solution to bake dry on the edge of a hot plate or by standing over night on the steam bath. Add 17 cc. of  $\text{HNO}_3$ , sp.gr. 1.42, and after digesting for a short time, add 85 cc. of hot water and heat to boiling for a few minutes. Allow the solution to stand for several hours at a temperature just below the boiling point. Filter off the precipitated  $\text{H}_2\text{SnO}_3$  on double closely woven filter papers, being careful to keep the solution hot throughout the process of filtration. Wash with boiling hot water. Receive the combined filtrate and washings in a 250 cc. beaker. Dilute to about 150 cc. with distilled water and insert electrodes. In the positive terminal use a sand-blasted platinum gauze electrode such as is used for the cathode in the determination of copper; in the negative terminal insert an electrode such as is used for the anode in the determination of copper. Cover with a pair of split watch glasses and electrolyze. For each solution use a current of 1.25 to 1.5 amperes at 10 volts continued for about one hour. Wash down the cover glasses, electrodes and sides of beaker, raising the level of the liquid slightly, and continue the electrolysis for 15 minutes. If no darkening of the newly exposed surface of the platinum can be detected the lead has been entirely deposited. Continue the electrolysis until no darkening of the platinum can be detected when the current has been passed for 15 minutes after the level of the liquid has been raised.

Interrupt the current once or twice for a few seconds during the course of the electrolysis in order to dissolve any metallic lead which may have been deposited on the negative terminal. When the lead has been entirely deposited, remove the anode quickly, rinse it in distilled water and then in alcohol, and dry it at  $210^\circ \text{C}$ . for one-half hour. Weigh as  $\text{PbO}_2$ , using the factor for lead 0.8643 instead of the theoretical value.

**Accuracy:** Duplicate determinations should check within 0.01 per cent of lead. Results obtained by this method are likely to be about 0.01 per cent too high. For exceptionally accurate or investigation work redissolve the coating from the electrode and determine the lead as sulfate. See the "Determination of Lead as Sulfate."

**Notes.** It is impossible to remove the tin quantitatively as  $\text{H}_2\text{SnO}_3$  in the case of alloys containing over 0.25 per cent of iron, and traces of tin are sometimes found in the  $\text{PbO}_2$  deposit. Small amounts of manganese also are occasionally deposited with the  $\text{PbO}_2$ . Tin and manganese are rarely present in the  $\text{PbO}_2$  in amounts which necessitate a purification of the deposit.

**Determination of Lead as Sulfate**

(For Samples Containing up to 0.2 Per Cent of Lead) (Optional)

**Solutions Required.** *Lead Acid:* Mix 300 cc. of  $\text{H}_2\text{SO}_4$ , sp.gr. 1.84, and 1800 cc. of distilled water. Dissolve 1 g. of lead acetate, c.p., in 300 cc. of distilled water and add this to the hot solution, stirring meanwhile. Let stand at least 24 hours and syphon through a thick asbestos filter.

*Dilute Alcohol for Washing:* Mix equal parts of denatured alcohol and distilled water.

**Method.** In a 250 cc. beaker dissolve 5 g. of bronze in 25 cc. of  $\text{HNO}_3$ , sp.gr. 1.42. Allow the solution to bake dry on the edge of a hot plate, or by standing over night on the steam bath. Add 17 cc. of  $\text{HNO}_3$ , sp.gr. 1.42, and after digesting for a short time, add 85 cc. of hot water and heat to boiling for a few minutes. Allow the solution to stand for several hours at a temperature just below the boiling point. Filter off the precipitated  $\text{H}_2\text{SnO}_3$  on double closely woven filter papers, being careful to keep the solution hot throughout the process of filtration. Wash with boiling hot water. To the combined filtrate and washings add 120 cc. of lead acid, and evaporate until copious fumes of  $\text{H}_2\text{SO}_4$  are evolved. Cool, add 105 cc. of distilled water to dissolve the salts and to make the acid concentration the same as in lead acid, heat to boiling and allow to cool and settle for 5 hours, or over night if convenient. Filter on a weighed porcelain gooch crucible and wash with lead acid. Wash out the lead acid with dilute alcohol, set the gooch crucible inside a porcelain crucible, dry and ignite for 5 minutes at the full heat of a Tirrell burner, cool and weigh as  $\text{PbSO}_4$ , which contains 68.29 per cent lead.

**Accuracy:** Duplicate determinations should check within 0.01 per cent of lead. Results obtained by this method are likely to be about 0.01 per cent too low.

**NOTE.** It is impossible to remove the tin quantitatively as  $\text{H}_2\text{SnO}_3$  in the case of alloys containing over 0.25 per cent of iron, but by the preliminary baking and long standing, most of the  $\text{H}_2\text{SnO}_3$  is precipitated.

**Determination of Copper and Lead Simultaneously by the Electrolytic Method**  
(For Samples Containing over 0.2 Per Cent of Lead)

**Method.** In a 150 cc. beaker dissolve 1 g. of bronze in 10 cc. of  $\text{HNO}_3$ , sp.gr. 1.42. When the action has ceased, evaporate the solution to dryness, and bake thoroughly on the edge of a hot plate. Add 10 cc. of  $\text{HNO}_3$ , sp.gr. 1.42, and after digesting for a short time add 50 cc. of distilled water, heat to boiling, and allow to stand and settle for about one hour, keeping the temperature just below the boiling point. Filter on double 7 cm. filter papers, keeping the solution hot, and receive the filtrate in a 200 cc. electrolysis beaker. Wash with boiling hot water, dilute to about 100 cc. and insert electrodes. In the positive terminal insert one of the platinum gauze anodes previously described, and in the negative terminal insert a platinum gauze cathode. Cover with a pair of split watch glasses and electrolyze, using a current of from 3 to 5 amperes at approximately 10 volts for each solution. After about 45 minutes the lead will have been entirely deposited on the anode as  $\text{PbO}_2$ ; without interrupting the current add to the electrolyte 3 to 4 cc. of  $\text{H}_2\text{SO}_4$ , sp.gr. 1.84, and continue the electrolysis. When the solution is colorless, wash down cover glasses, electrodes and sides of beaker, raising the level of the liquid slightly, and continue the passage of the current about 15 minutes, noting whether or not copper is deposited on the newly exposed surface of the platinum. If no copper appears, transfer about 1 cc. of the colorless solution to the cavity of a porcelain test plate, and add a few drops of fresh  $\text{H}_2\text{S}$  water. If the slightest discoloration occurs continue the electrolysis until there is no discoloration whatever upon repeating the test. Remove the solution from the electrodes quickly without interrupting the current. Rinse the electrodes in distilled water and then dip them in two successive baths of alcohol. Dry the anode at  $210^\circ \text{C}$ . for one-half hour. Weigh as  $\text{PbO}_2$ , using the factor for lead 0.8643 instead of the theoretical value. Shake off the excess alcohol from the cathode and ignite the remainder by bringing it to the flame of an alcohol lamp. Keep the cathode moving continually while the alcohol burns. Weigh as metallic copper.

**Accuracy:** Duplicate copper determinations should check within 0.10 per cent of copper. Duplicate lead determinations should check within 0.02 per cent of lead. Lead results obtained by this method are likely to be about 0.01 per cent too high.

**Determination of Tin**

**Solutions Required.** *Dilute Hydrochloric Acid:* Mix 500 cc. of HCl, sp.gr. 1.20, and 500 cc. of distilled water.

*Dilute Sulfuric Acid:* Mix 300 cc. of  $\text{H}_2\text{SO}_4$ , sp.gr. 1.84, and 600 cc. of distilled water.

*Dilute Ammonia:* Mix 100 cc. of  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, and 900 cc. of distilled water.

*Ammonium Acetate Solution for Washing:* Dissolve 10 g. of ammonium acetate in 300 cc. of distilled water. Make slightly acid with acetic acid and saturate with  $\text{H}_2\text{S}$  gas.

**Method.** In a 150 cc. beaker dissolve 2 g. of bronze in a mixture of 10 cc. of HCl, sp.gr. 1.20, and 5 cc. of  $\text{HNO}_3$ , sp.gr. 1.42. Dilute to about 75 cc. with distilled water. Add  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, until the basic salts of copper have dissolved and the solution has become a deep blue. Boil and allow to settle, and filter on a closely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute HCl. Dilute the solution to about 100 cc. Add  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, until a permanent precipitate forms. Heat the solution to boiling, allow to settle, filter and wash as before. Dissolve the precipitate on the filter with boiling hot dilute  $\text{H}_2\text{SO}_4$ , washing the paper very thoroughly with this acid. Add  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, cautiously until the precipitate which forms at first dissolves rather slowly. Allow the solution to stand for some hours and if any lead sulfate forms filter it off. Dilute the solution to about 200 cc. and saturate it with  $\text{H}_2\text{S}$  gas. Filter the precipitated tin sulfide off on double papers and wash with ammonium acetate solution, retaining the filtrate and washings from the iron determination. Dry the precipitate and place it with the papers in a porcelain crucible which projects part way through a hole in a piece of asbestos board. Heat slowly until any free sulfur has been driven off, but without allowing the sulfur to burn. When the sulfur has been expelled, place the crucible on a triangle and ignite slowly at first and finally at the full heat of the burner. If the precipitate weighs more than 20 mg. heat to constant weight, using a blast lamp. Weigh as  $\text{SnO}_2$ , which contains 78.81 per cent of tin.

**Accuracy:** Duplicate determinations should check within 0.06 per cent of tin.

**NOTES.** If, during ignition, the sulfur is allowed to burn, some tin sulfate may be formed, causing high results. On the other hand, low results may be caused by too high heat, which causes spattering and volatilizes some tin sulfide.

Tin and iron are best determined on the same sample, retaining the filtrate from the tin sulfide precipitate to use for the iron determination.

**Determination of Iron**

**Solutions Required.** See "Determination of Tin," and the following:

*Dilute Sulfuric Acid for Reductor:* Mix 500 cc. of  $H_2SO_4$ , sp.gr. 1.84, and 500 cc. of distilled water.

*Potassium Permanganate:* Dissolve 0.2 g. of  $KMnO_4$  in water, filter through asbestos, and dilute to 1000 cc. with distilled water. Standardize against 0.020 g. portions of pure sodium oxalate: or, standardize against 0.020 g. portions of purest iron wire. Each cubic centimeter is equivalent to approximately 0.00033 g. of iron.

**Method.** Proceed exactly as in the "Determination of Tin" through the filtration and washing of the precipitated tin sulfide. Combine the filtrate and washings from the tin sulfide precipitate and boil until all  $H_2S$  is expelled. Add  $HNO_3$ , sp.gr. 1.42, until the iron is oxidized, which is shown by the solution becoming clear and of a yellowish color. Add about 5 g. of  $NH_4Cl$ , then  $NH_4OH$ , sp.gr. 0.90 until a permanent precipitate forms. Boil, allow to settle, filter on a loosely woven filter paper and wash with dilute ammonia and with hot water. Dissolve the precipitate on the paper with hot dilute  $HCl$  and add  $NH_4OH$ , sp.gr. 0.90 to the solution again until a permanent precipitate forms. Boil, allow to settle, filter on a loosely woven filter paper, and wash with dilute ammonia and with hot water as before. Dissolve the precipitate on the filter with dilute  $H_2SO_4$ , transfer the solution to a Jones reductor, and add 40 cc. of the dilute  $H_2SO_4$  used for the reductor. Pass the solution through the reductor, wash first with 150 cc. of distilled water and then with an additional 100 cc. of distilled water, and titrate with the standard  $KMnO_4$ .

**Accuracy:** Duplicate determinations should check within 0.03 per cent of iron.

**Notes.** A blank determination should be made on corresponding amounts of acid and water passed through the reductor and the results should be corrected accordingly. About 0.5 cc. of the permanganate will be required to give a permanent coloration to the solution.

A small quantity of liquid should always be left in the reductor funnel, and air should never be allowed to enter the body of the reductor.

A description and further details of use of reductor see Vol. I, pages 319, 320.

**Determination of Manganese by the Persulfate Method**

**Solutions Required.** *Solution for Dissolving:* Mix 500 cc. of  $\text{H}_2\text{SO}_4$ , sp.gr. 1.84, 200 cc. of  $\text{HNO}_3$ , sp.gr. 1.42, and 1700 cc. of distilled water.

*Silver Nitrate:* Dissolve 1.33 g. of  $\text{AgNO}_3$  in 1000 cc. of distilled water.

*Stock Sodium Arsenite:* To 15 g. of arsenious oxide ( $\text{As}_2\text{O}_3$ ) in a 300 cc. Erlenmeyer flask, add 45 g. of  $\text{Na}_2\text{CO}_3$  and 150 cc. of distilled water. Heat the flask and contents on the steam bath until the  $\text{As}_2\text{O}_3$  is dissolved. Cool the solution, filter and make up to 1000 cc. with distilled water.

*Standard Sodium Arsenite:* Mix 200 cc. of stock sodium arsenite solution with 2500 cc. of distilled water, and standardize against a steel or iron of known manganese content as determined by the Bismuthate Method, or standardize against one of the Bureau of Standards' standard irons or steels. One cc. of this solution should be equivalent to approximately 0.00050 g. of manganese.

*Ammonium Persulfate:* Dissolve 60 g. of ammonium persulfate in 1000 cc. of distilled water.

**Method.** In a 250 cc. Erlenmeyer flask dissolve 1 g. of bronze in 24 cc. of the "solution for dissolving." Allow to stand on a steam bath or hot plate until entirely dissolved, and until the oxides of nitrogen are expelled. Add 15 cc. of  $\text{AgNO}_3$  solution and 20 cc. of ammonium persulfate and leave on the steam bath until the solution has developed a full permanganate color and no bubbles can be seen to come off when the flask is given a whirling motion. Cool to below  $25^\circ\text{C}$ . in running water, and add 50 cc. of cold water. Titrate with standard sodium-arsenite solution to the disappearance of the pink color.

**Accuracy:** Duplicate determinations should check within 0.02 per cent of manganese.

**NOTES.** Large amounts of permanganic acid are unstable; on that account samples which contain large amounts of manganese should have correspondingly small samples weighed out. For instance, with metal containing 1.5 per cent of manganese use a 0.10 g. sample, while if metal contains 0.75 per cent manganese use a 0.20 g. sample.

The solution must be cold when it is titrated, for high temperatures cause low results to be obtained.

**Determination of Manganese by the Bismuthate Method  
(Optional)**

**Solutions Required.** *Nitric Acid* (1 : 3): Mix 250 cc. of  $\text{HNO}_3$  sp.gr. 1.42, and 750 cc. of distilled water.

*Nitric Acid for Washing:* Mix 30 cc. of  $\text{HNO}_3$  sp.gr. 1.42 and 970 cc. of distilled water.

*Ferrous Ammonium Sulfate:* Dissolve 12.4 g. of ferrous ammonium sulfate crystals in 950 cc. of distilled water, and add 50 cc. of  $\text{H}_2\text{SO}_4$  sp.gr. 1.84.

*Potassium Permanganate:* Dissolve 1 g. of  $\text{KMnO}_4$  in 1000 cc. of distilled water. Allow it to stand for about one week and then filter it through asbestos. Standardize against 0.10 g. portions of pure sodium oxalate.

**Method.** In a 250 cc. Erlenmeyer flask dissolve 1 g. of bronze in 50 cc. of  $\text{HNO}_3$  (1 : 3). Without filtering off the  $\text{H}_2\text{SnO}_3$ , cool and add 0.5 g. of sodium bismuthate. Heat for a few minutes until the purple color has disappeared, with or without the precipitation of manganese dioxide. Add a little ferrous-ammonium sulfate solution until the solution becomes clear, and boil until the oxides of nitrogen are expelled. Cool, add an excess of sodium bismuthate and agitate for a few minutes. Add 50 cc. of  $\text{HNO}_3$  for washing and filter through an alundum crucible or an asbestos pad. Wash with 50 cc. of the  $\text{HNO}_3$  for washing. Add from a pipette or a burette 10 cc. of ferrous-ammonium sulfate solution and titrate with  $\text{KMnO}_4$ . Owing to the presence of considerable copper, the end point is somewhat different from the normal pink color.

In exactly the same manner carry through a blank determination, using the same amounts of  $\text{HNO}_3$  and sodium bismuthate as was done with the regular sample. Finally add exactly 10 cc. of ferrous-ammonium sulfate solution and titrate with  $\text{KMnO}_4$ . The difference between the two titrations is due to the manganese. Since one manganese as permanganate oxidized five irons, the iron value of the permanganate multiplied by the factor ( $\text{Mn}/5 \text{ Fe}$ ) (or 0.1967) gives the value in terms of manganese.

**Accuracy:** Duplicate determinations should check within 0.02 per cent of manganese.

**Notes.** Instead of employing the method of reducing the permanganic acid by means of standardized ferrous ammonium sulfate solution and titrating the excess of this reagent, it is possible to reduce the permanganic acid by standard sodium arsenite solution. See "Determination of Manganese by the Persulfate Method."

The filtrate from the bismuthate must be perfectly clear, as the least particle of bismuthate carried into the filtrate will vitiate the results.



**Analysis of Gun Metal***Standard Method, A. S. T. M.*

**General Considerations.** Phosphorus should not be present in this alloy except in very small amounts. A rapid qualitative test for it is given whereby it is easily seen whether or not it is necessary to make a correction for its presence in the determination of tin.

A special method is also given for the determination of tin in alloys such as phosphor-bronze which contain considerable phosphorus.

**Alloy of Copper, Tin, Lead, Iron and Zinc****Determination of Copper by the Electrolytic Method**

**Apparatus for Electrolysis.** *Electrodes:* The electrodes recommended are of the stationary and not of the rotating type, as the stationary require less operator's time and there is less chance for erroneous results to be obtained than with the other kind. Rapid and accurate results are obtained with stationary electrodes made from platinum gauze.

*Cathodes:* Platinum cathodes may be formed either from plain or perforated sheets, or from wire gauze, and may be either open or closed cylinders. They should give a depositing surface, counting both sides, of approximately 100 sq. cm. Gauze cathodes are recommended, and are best made from gauze containing approximately 400 meshes per sq. cm. (45 meshes per linear inch). The cathode should be stiffened by doubling the gauze for about 3 mm. at the top and at the bottom of the cylinder. The cylinder should be approximately 30 mm. in diameter and 30 mm. in height. The stem should be made from 1.14 mm. or 1.29 mm. wire, flattened and welded the entire width of the gauze; the height over all should be approximately 130 mm., and the gauze should be sand blasted.

*Anodes:* Platinum anodes may be of the spiral type when used in the determination of copper by electrolysis, or in the electrolytic determination of lead when it is present in amounts not over 0.2 per cent. When used in electrolytic determination of copper and lead together in samples containing 0.2 per cent lead or over, the anodes should be of wire gauze. Spiral anodes should be made from 1.02 mm. or 1.14 mm. wire formed into a spiral of 7 turns having a height of approximately 51 mm. and a diameter of 16 mm., the length over all being approximately 145 mm. Platinum gauze used in making anodes should contain approximately 400 meshes per sq. cm. (45 meshes per linear inch). The gauze should be formed into closed cylinders approximately 12 mm. in diameter and 30 mm. in height. The cylinders should be stiffened by doubling the gauze for about 3 mm. at the top and at the bottom. The stem should be made from 1.02 mm. or 1.29 mm. wire, flattened and welded the entire width of the gauze; the height over all should be approximately 137 mm., and the gauze should be sand blasted.

**Method.** In a 150 cc. beaker dissolve 1 g. of gun metal in 10 cc. of  $\text{HNO}_3$ , sp.gr. 1.42. When the action has ceased, boil until the oxides of nitrogen are expelled, add 50 cc. of distilled water, and allow to stand and settle for about one hour, keeping the temperature just below the boiling point. Filter on double 7 cm. ashless papers, being careful to keep the solution hot throughout the process of filtration, and receiving the filtrate in a 200 cc. beaker of the

tall type used in electrolysis. Wash with boiling hot water. Retain the papers containing the precipitate for subsequent use in the tin determination.

Add to the filtrate 5 cc. of  $H_2SO_4$ , sp.gr. 1.84, and determine copper by electrolysis, retaining the electrolyte, after the removal of the copper, for the subsequent determination of zinc. See the "Determination of Copper by the Electrolytic Method," Chemical Analysis of Manganese Bronze, page 1089.

**Accuracy:** Duplicate determinations should check within 0.10 per cent of copper.

**Notes.** Copper, zinc, and tin are conveniently determined on the same sample, tin being first removed, and any zinc tested for after copper has been deposited by electrolysis.

If the solution becomes cool during the first filtration some of the metastannic acid ( $H_2SnO_3$ ) may dissolve.

#### Determination of Tin (For Samples Free from Phosphorus)

**Method.** See the "Determination of Copper by the Electrolytic Method."

Use the papers containing the  $H_2SnO_3$ , which was filtered off in the Determination of Copper by the Electrolytic Method. Ignite the papers with the precipitate, while moist, in a porcelain or platinum crucible, slowly at first, and finally at the full heat of the burner. If the precipitate weighs more than 20 mg. heat to constant weight, using a blast lamp. Weigh as  $SnO_2$ , which contains 78.81 per cent of tin.

**Accuracy:** Duplicate determinations should check within 0.04 per cent of tin.

This method is not accurate for alloys which contain arsenic, antimony or phosphorus, or which contain over 0.25 per cent of iron. The  $SnO_2$  may be contaminated with a slight amount of copper and purification is required in very accurate work, but is generally neglected in routine analysis.

The ignited tin oxide contains the phosphorus which may be present in the alloy. The following test is here made use of to detect phosphorus and to estimate its amount, if any is found.

#### Qualitative Test for Phosphorus

**Solutions Required.** *Ferric Chloride:* Dissolve 25 g. of ferric chloride in 100 cc. of distilled water, and add 25 cc. of  $HCl$ , sp.gr. 1.20.

**Method.** Dip a small piece of the alloy into a few cubic centimeters of ferric chloride for about 10 seconds, and then rinse it in running water. Alloys containing phosphorus are darkened noticeably where they have been dipped; alloys containing over 0.25 per cent of phosphorus are rendered almost black by this test. Arsenic and antimony act in a manner similar to phosphorus, but should not be present in this alloy.

**Correction for Phosphorus.** In alloys containing up to 0.20 per cent of phosphorus a correction for its presence in the ignited tin oxide may be made according to the following empirical method. From the phosphorus content of the alloy, which must be determined on a separate sample, compute the weight of  $P_2O_5$  and subtract two-thirds of this weight from the weight of the ignited tin oxide containing phosphorus. The remainder is considered as pure  $SnO_2$ , which contains 78.81 per cent of tin. The factor for converting phosphorus to  $\frac{2}{3} \times P_2O_5$  is 152.6 per cent or approximately one and one-half times the phosphorus content of the sample.

If the alloy contains over 0.20 per cent of phosphorus a special method for the determination of tin should be used.

Arsenic and antimony should not be present in weighable amounts in the tin oxide resulting from a sample of gun metal.

Iron may be present in the  $H_2SnO_3$  in very small amounts, but its weight is negligible in this determination.

In alloys which contain over 0.25 per cent of iron, use the method for the Determination of Tin in Manganese Bronze, Standard Method for Chemical Analysis of Manganese Bronze, page 1094.

#### **Determination of Tin (For Samples Containing Phosphorus)**

**Solutions Required.** *Yellow Ammonium Sulfide:* Saturate 200 cc. of  $NH_4OH$ , sp.gr. 0.90 with  $H_2S$  gas. Dissolve in this solution 3 or 4 g. of sulfur flour and about 1 g. of  $NH_4Cl$ . Make up this solution freshly and filter immediately before using.

*Dilute Yellow Ammonium Sulfide for Washing:* Mix 20 cc. of yellow ammonium sulfide, prepared as above, and 400 cc. of distilled water.

*Ammonium Acetate for Washing:* Dissolve 10 g. of ammonium acetate in 300 cc. of distilled water, make slightly acid with acetic acid and saturate with  $H_2S$  gas.

**Method.** See the "Determination of Copper by the Electrolytic Method."

Use the papers containing the freshly filtered  $H_2SnO_3$ , which was filtered off in the Determination of Copper by the Electrolytic Method. Transfer the papers with the precipitate to a 150 cc. beaker, and cover them with 40 to 50 cc. of yellow ammonium sulfide. Warm for about 15 minutes, or until the  $H_2SnO_3$  has dissolved. Filter and wash thoroughly with dilute yellow ammonium sulfide. Acidify the combined filtrate and washings cautiously with 50 per cent acetic acid. Warm, and allow the precipitated tin sulfide and sulfur to settle. Filter on double papers and wash with ammonium acetate solution. Dry the precipitate, and place it with the papers in a porcelain crucible which projects part way through a hole in a piece of asbestos board. Heat slowly until the free sulfur has been driven off, but without allowing the sulfur to burn. When the sulfur has been expelled, place the crucible on a triangle and ignite slowly at first, and finally at the full heat of the burner. If the precipitate weighs more than 20 mg. heat to constant weight, using a blast lamp. Weigh as  $SnO_2$ , which contains 78.81 per cent tin.

**Accuracy:** Duplicate determinations should check within 0.06 per cent of tin.

**NOTES.** If during the first filtration the solution becomes cool, some of the  $H_2SnO_3$  may dissolve.

During ignition, if the sulfur is allowed to burn, some tin sulfate may be formed, causing high results. On the other hand, low results may be caused by too high heat, which causes spattering, and volatilizes some tin sulfide.

#### Determination of Lead by the Electrolytic Method (For Samples Containing up to 0.2 Per Cent of Lead)

**Method.** In a 250 cc. beaker dissolve 5 g. of gun metal in 25 cc. of  $HNO_3$ , sp.gr. 1.42. Allow the solution to bake dry on the edge of a hot plate or by standing over night on the steam bath. Add 17 cc. of  $HNO_3$ , sp.gr. 1.42, and after digesting for a short time, add 85 cc. of hot water and heat to boiling for a few minutes. Allow the solution to stand for several hours at a temperature just below the boiling point. Filter off the precipitated  $H_2SnO_3$  on double closely woven filter papers, being careful to keep the solution hot throughout the process of filtration. Wash with boiling hot water. Receive the combined filtrate and washings in a 250 cc. beaker. Dilute to about 150 cc. with distilled water and insert electrodes. In the positive terminal use a sand-blasted platinum gauze electrode such as is used for the cathode in the determination of copper; in the negative terminal insert an electrode such as is used for the anode in the determination of copper. Cover with a pair of split watch glasses and electrolyze. For each solution use a current of 1.25 to 1.5 amperes at 10 volts continued for about one hour. Wash down the cover glasses, electrodes and sides of beaker, raising the level of the liquid slightly, and continue the electrolysis for 15 minutes. If no darkening of the newly exposed surface of the platinum can be detected the lead has been entirely deposited. Continue the electrolysis until no darkening of the platinum can be detected when the current has been passed for 15 minutes after the level of the liquid has been raised.

Interrupt the current once or twice for a few seconds during the course of the electrolysis in order to dissolve any metallic lead which may have been deposited on the negative terminal. When the lead has been entirely deposited, remove the anode quickly, rinse it in distilled water and then in alcohol, and dry it at  $210^{\circ}\text{C}$ . for one-half hour. Weigh as  $\text{PbO}_2$ , using the factor for lead 0.8643 instead of the theoretical value.

**Accuracy:** Duplicate determinations should check within 0.01 per cent of lead. Results obtained by this method are likely to be about 0.01 per cent too high. For exceptionally accurate or investigation work redissolve the coating from the electrode and determine the lead as sulfate. See the "Determination of Lead as Sulfate."

**NOTES.** It is impossible to remove the tin quantitatively as  $\text{H}_2\text{SnO}_3$  in the case of alloys containing over 0.25 per cent of iron, and traces of tin are sometimes found in the  $\text{PbO}_2$  deposit. Small amounts of manganese also are occasionally deposited with the  $\text{PbO}_2$ . Tin and manganese are rarely present in the  $\text{PbO}_2$  in amounts which necessitate a purification of the deposit.

#### Determination of Lead as Sulfate

(For Samples Containing up to 0.2 Per Cent of Lead) (Optional)

**Solutions Required.** *Lead Acid:* Mix 300 cc. of  $\text{H}_2\text{SO}_4$ , sp.gr. 1.84, and 1800 cc. of distilled water. Dissolve 1 g. of lead acetate, c.p., in 300 cc. of distilled water and add this to the hot solution, stirring meanwhile. Let stand at least 24 hours and syphon through a thick asbestos filter.

*Dilute Alcohol for Washing:* Mix equal parts of denatured alcohol and distilled water.

**Method.** In a 250 cc. beaker dissolve 5 g. of gun metal in 25 cc. of  $\text{HNO}_3$ , sp.gr. 1.42. Allow the solution to bake dry on the edge of a hot plate, or by standing over night on the steam bath. Add 17 cc. of  $\text{HNO}_3$ , sp.gr. 1.42, and after digesting for a short time, add 85 cc. of hot water and heat to boiling for a few minutes. Allow the solution to stand for several hours at a temperature just below the boiling point. Filter off the precipitated  $\text{H}_2\text{SnO}_3$  on double closely woven filter papers, being careful to keep the solution hot throughout the process of filtration. Wash with boiling hot water. To the combined filtrate and washings add 120 cc. of lead acid, and evaporate until copious fumes of  $\text{H}_2\text{SO}_4$  are evolved. Cool, add 105 cc. of distilled water to dissolve the salts and to make the acid concentration the same as in lead acid, heat to boiling, and allow to cool and settle for 5 hours, or over night if convenient. Filter on a weighed porcelain gooch crucible and wash with lead acid. Wash out the lead acid with dilute alcohol, set the gooch crucible inside a porcelain crucible, dry and ignite for 5 minutes at the full heat of a Tirrill burner, cool and weigh as  $\text{PbSO}_4$ , which contains 68.29 per cent lead.

**Accuracy:** Duplicate determinations should check within 0.01 per cent of lead. Results obtained by this method are likely to be about 0.01 per cent too low.

**NOTE.** It is impossible to remove the tin quantitatively as  $H_2SnO_3$  in the case of alloys containing over 0.25 per cent of iron, but by the preliminary baking and long standing, most of the  $H_2SnO_3$  is precipitated.

#### Determination of Zinc

**Solutions Required.** *Dilute Hydrochloric Acid:* Mix 500 cc. of HCl, sp.gr. 1.20 and 500 cc. of distilled water.

**Method.** See the "Determination of Copper by the Electrolytic Method."

After the copper has been completely deposited by electrolysis, quickly remove the cathode and wash it thoroughly in distilled water, catching the washings in the beaker containing the electrolyte. Heat the solution and saturate with  $H_2S$  gas. Filter off any precipitate, and boil the solution to expel  $H_2S$ . Make the solution barely alkaline with  $NH_4OH$ , and add 25 cc. of 85 per cent formic acid. Dilute the solution with distilled water to 300 cc. heat to boiling, and saturate with  $H_2S$  gas. Filter and wash with hot water. Dissolve the precipitate with hot dilute HCl, and transfer the solution to a weighed platinum or porcelain dish or crucible. Add a few drops of  $H_2SO_4$ , sp.gr. 1.84, and evaporate the solution until copious fumes escape. If the solution is not clear and colorless, cool, add a few cubic centimeters of  $HNO_3$ , sp.gr. 1.42 and again evaporate the solution until fumes of  $H_2SO_4$  come off freely. Repeat the treatment with  $HNO_3$  if necessary, until the organic matter is destroyed, and the solution is colorless. Remove the excess of  $H_2SO_4$  by heating the dish cautiously, and finally heat to dull redness. Weigh as zinc sulfate, which contains 40.49 per cent of zinc.

**Accuracy:** Duplicate determinations should check within 0.05 per cent of zinc.

#### Determination of Phosphorus by the Alkalimetric Method

**Solutions Required.** *Nitric Acid for Dissolving:* Mix 1000 cc. of  $HNO_3$ , sp.gr. 1.42 and 1200 cc. of distilled water.

*Nitric Acid for Washing:* Mix 20 cc. of  $HNO_3$ , sp.gr. 1.42, and 1000 cc. of distilled water.

*Ammonium Molybdate:* Solution No. 1. Place in a beaker 100 g. of 85 per cent molybdic acid, mix it thoroughly with 240 cc. of distilled water, add 140 cc. of  $NH_4OH$ , sp.gr. 0.90, filter and add 60 cc. of  $HNO_3$ , sp.gr. 1.42.

Solution No. 2. Mix 400 cc. of  $HNO_3$ , sp.gr. 1.42 and 960 cc. of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly; then add 0.1 g. of ammonium phosphate dissolved in 10 cc. of distilled water and let stand at least 24 hours before using.

*Potassium Nitrate, 1 per cent:* Dissolve 10 g. of  $\text{KNO}_3$  in 1000 cc. of distilled water.

*Phenolphthalein Indicator:* Dissolve 0.2 g. of phenolphthalein in 50 cc. of 95 per cent ethyl alcohol and 50 cc. of distilled water.

*Standard Sodium Hydroxide:* Dissolve 6.5 g. of purified  $\text{NaOH}$  in 1000 cc. of distilled water, add a slight excess of 1 per cent solution of barium hydroxide, let stand for 24 hours, decant the liquid, and standardize it against a steel of known phosphorus content as determined by the molybdate-magnesia method, so that 1 cc. will be equivalent to 0.01 per cent of phosphorus on the basis of a 2 g. sample (see notes).

Protect the solution from carbon dioxide with a soda-lime tube.

*Ferric Chloride:* Dissolve 100 g. of ferric chloride (phosphorus free) in 100 cc. of distilled water.

*Standard Nitric Acid:* Mix 10 cc. of  $\text{HNO}_3$ , sp.gr. 1.42, and 1000 cc. of distilled water. Titrate the solution against standardized  $\text{NaOH}$ , using phenolphthalein as indicator, and make it equivalent to the  $\text{NaOH}$  by adding distilled water.

**Method.** In a 400 cc. casserole dissolve 1 g. of gun metal in 10 cc. of  $\text{HNO}_3$ , sp.gr. 1.42. Add 20 cc. of  $\text{HCl}$ , sp.gr. 1.20, and evaporate to dryness. Moisten with  $\text{HCl}$ , evaporate to dryness again, and bake to dull redness. Moisten with  $\text{HCl}$  again, add 3 cc. of ferric chloride solution, and dilute to about 200 cc. with distilled water. Add  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, until the basic salts of copper have dissolved and the solution has become a deep blue. Boil, allow to settle, and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute  $\text{HCl}$ , dilute the solution to about 200 cc., add  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, until the precipitate which forms at first dissolves rather slowly, and saturate with  $\text{H}_2\text{S}$  gas. Filter off and reject the precipitate. Boil the filtrate to expel  $\text{H}_2\text{S}$ , and add  $\text{HNO}_3$ , sp.gr. 1.42, until the iron is oxidized. Add  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, until the solution is alkaline. Boil and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with  $\text{HNO}_3$  (sp. gr. 1.42) receiving the solution in a 350 cc. Erlenmeyer flask. Add  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, until the iron is entirely precipitated, and then add  $\text{HNO}_3$ , sp.gr. 1.42, cautiously until the solution just becomes clear. Bring the solution to a temperature of about  $80^\circ \text{C}$ ., and add 40 cc. of ammonium molybdate at room temperature. Allow to stand for one minute, shake or agitate for 3 minutes, and filter on a 9 cm. paper. Wash the precipitate three times with the 2 per cent  $\text{HNO}_3$  solution to free it from iron, and continue the washing with the 1 per cent  $\text{KNO}_3$  solution until the precipitate and flask are free from acid.

Transfer the paper and precipitate to a solution flask, add 20 cc. of distilled water, 5 drops of phenolphthalein solution as indicator, and an excess of standard NaOH solution. Insert a rubber stopper and shake vigorously until solution of the precipitate is complete. Wash off the stopper with distilled water and determine the excess of NaOH solution by titrating with standard  $\text{HNO}_3$  solution. Each cubic centimeter of standard NaOH solution represents 0.01 per cent of phosphorus.

**Accuracy:** Duplicate determinations should check within 0.01 per cent of phosphorus.

**Notes.** The ammonium-molybdate solution should be kept in a cool place and should always be filtered before using.

All distilled water used in titrations should be freed from carbon dioxide by boiling or otherwise.

Bureau of Standards Standard Steel No. 19 (a) is recommended as a suitable steel for standardisation of the NaOH solution.

#### Determination of Phosphorus by the Ferric-Alum Method (Optional)

**Solutions Required.** *Ferric Chloride:* Dissolve 100 g. of ferric chloride (phosphorus free) in 100 cc. of distilled water.

*Dilute Ammonia:* Mix 100 cc. of  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, and 900 cc. of distilled water.

*Dilute Hydrochloric Acid:* Mix 500 cc. of  $\text{HCl}$ , sp.gr. 1.20, and 500 cc. of distilled water.

*Dilute Sulfuric Acid for Dissolving:* Mix 200 cc. of  $\text{H}_2\text{SO}_4$ , sp.gr. 1.84, and 800 cc. of distilled water.

*Dilute Sulfuric Acid for Reductor:* Mix 500 cc. of  $\text{H}_2\text{SO}_4$ , sp.gr. 1.84, and 500 cc. of distilled water.

*Ammonium Molybdate:* Solution No. 1. Place in a beaker 100 g. of 85 per cent molybdic acid, mix it thoroughly with 240 cc. of distilled water, add 140 cc. of  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, filter and add 60 cc. of  $\text{HNO}_3$ , sp.gr. 1.42.

Solution No. 2. Mix 400 cc. of  $\text{HNO}_3$ , sp.gr. 1.42, and 960 cc. of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly, then add 0.1 g. of ammonium phosphate dissolved in 10 cc. of distilled water, and let stand at least 24 hours before using.

*Acid Ammonium Sulfate:* Mix 25 cc. of  $\text{H}_2\text{SO}_4$ , sp.gr. 1.84, and 1000 cc. of distilled water, and then add 15 cc. of  $\text{NH}_4\text{OH}$ , sp.gr. 0.90.

*Ferric Alum:* Dissolve 200 g. of ferric ammonium sulfate crystals in 1950 cc. of distilled water. Add 50 cc. of  $\text{H}_2\text{SO}_4$ , sp.gr. 1.84, and 80 cc. of phosphoric acid, 85 per cent.

*Potassium Permanganate:* Dissolve from 3.0 to 3.2 g. of  $\text{KMnO}_4$  in 1000 cc. of distilled water. Allow the solution to stand for about one week, and then filter it through an asbestos filter. Standardize by using about 0.200 g. portions of pure sodium oxalate.



**Method.** In a 400 cc. casserole dissolve 1 g. of gun metal in 10 cc. of  $\text{HNO}_3$ , sp.gr. 1.42. Add 20 cc. of  $\text{HCl}$ , sp.gr. 1.20, and evaporate to dryness. Moisten with  $\text{HCl}$ , evaporate to dryness again, and bake to dull redness. Moisten with  $\text{HCl}$  again, add 3 cc. of ferric chloride solution, and dilute to about 200 cc. with distilled water. Add  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, until the basic salts of copper have dissolved and the solution has become a deep blue. Boil, allow to settle, and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute  $\text{HCl}$ , dilute the solution to about 200 cc., add  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, until the precipitate which forms at first dissolves rather slowly, and saturate with  $\text{H}_2\text{S}$  gas. Filter off and reject the precipitate. Boil the filtrate to expel  $\text{H}_2\text{S}$ , and add  $\text{HNO}_3$ , sp.gr. 1.42, until the iron is oxidized. Add  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, until the solution is alkaline. Boil and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute  $\text{H}_2\text{SO}_4$ , receiving the solution in a 350 cc. Erlenmeyer flask. Add  $\text{NH}_4\text{OH}$ , sp.gr. 0.90, until the iron is entirely precipitated, and then add  $\text{HNO}_3$ , sp.gr. 1.42, cautiously until the solution just becomes clear. Bring the solution to a temperature of about  $80^\circ \text{C}$ ., and add 40 cc. of ammonium molybdate at room temperature. Allow to stand for one minute, shake or agitate for 3 minutes, filter on a 9 cm. paper, and wash very thoroughly (about 25 times) with acid ammonium sulfate. Dissolve the precipitate on the paper using 50 cc. of dilute ammonia. Add 10 cc. of  $\text{H}_2\text{SO}_4$ , sp.gr. 1.84, and immediately pass the solution through a Jones reductor, which has the reductor tube prolonged and reaching nearly to the bottom of the flask, dipping into 50 cc. of ferric-alum solution. Wash through the reductor with 150 cc. of distilled water, and follow with an additional 100 cc. of distilled water. Titrate with standard  $\text{KMnO}_4$ .

By this method the molybdenum in passing through the reductor is reduced entirely to the form  $\text{Mo}_2\text{O}_3$ , and is oxidized by the ferric alum to the form  $\text{MoO}_3$ , an equivalent amount of iron being reduced to the ferrous condition. As the yellow precipitate contains one atom of phosphorus to each twelve molecules of  $\text{MoO}_3$ , and as three atoms of oxygen oxidize two of molybdenum, eighteen oxygens or thirty-six irons are equivalent to one phosphorus. Therefore, the iron value of the permanganate multiplied by the factor  $\text{P}/36 \text{ Fe}$  (or 0.01540) gives the value of the permanganate in terms of phosphorus.

**Accuracy:** Duplicate determinations should check within 0.01 per cent of phosphorus.

**NOTES.** The ammonium-molybdate solution should be kept in a cool place and should always be filtered before using.

A blank determination should be made on corresponding amounts of acid and water, passing through the reductor into the usual amount of ferric-alum solution in the flask.

A small quantity of liquid should always be left in the reductor funnel, and air should never be allowed to enter the reductor.

Description of the Jones reductor is given on page 319, Volume I.

### MERCURY IN ZINC AMALGAM

The following method is used by the N. Y., N. H. and H. Railroad for determining mercury in zinc amalgams of battery zines:

**Procedure.** Four to 5 grams of alloy filings are dissolved in about 75 cc. of HCl (1 : 1) and boiled for about 3 hrs. Zinc dissolves and is filtered off, leaving lead and mercury as metals. The washed residue is dried in a porcelain crucible at 100° C., then cooled and weighed. The metals are now heated to dull redness (Hood) and the residue of lead again weighed. The loss of weight is due to the volatilized mercury.

# FIXED OILS, FATS AND WAXES

AUGUSTUS H. GILL<sup>1</sup>

It will be remembered that the *fixed oils* are those which leave a permanent stain on paper, whereas the essential or volatile oils evaporate. The fixed oils, if saponifiable, are glycerides of the higher fatty acids, oleic,  $C_{17}H_{33}COOH$ , stearic,  $C_{17}H_{35}COOH$ , palmitic,  $C_{16}H_{33}COOH$ ; and if unsaponifiable, hydrocarbons, usually of the paraffin ( $C_nH_{2n+2}$ ) and olefin ( $C_nH_{2n}$ ) series. The *fats* differ from the oils in having a higher melting-point, caused by a larger percentage of stearic and palmitic acid. The *waxes* differ from the oils or fats in that the former are esters of monatomic alcohols. The oils are further divided according to their drying power on exposure to the air, into drying, semi-drying and non-drying oils.

The drying oils contain a large proportion of glycerides of the unsaturated acids, particularly linoleic and linolenic, whereas the semi-drying contain a smaller percentage, and the non-drying little or none of these esters.

## Examination of an Unknown Oil

There being no specific tests for the various oils, as for their identification, the analyst should, in attacking an unknown oil, ascertain all possible facts about it, as the source, the use to which it is put, and the cost.

Certain physical properties too, may aid in the examination. The *color* is of little assistance, as oils may be colored by the use of oleates or butyrates of iron or copper. *Fluorescence* or "bloom" is valuable as indicating the presence of mineral oil; this can be shown by placing a few drops of the oil on a sheet of ebonite and observing the bluish color. The *odor* and *taste* are particularly valuable. Marine animal oils are detected, especially when warm, by their strong "fishy" odor, while neatsfoot, tallow, lard, rosin and linseed oils each have a well-marked and easily distinguishable smell. Whale oil is said to have a "nutty," and rape oil has a harsh, unpleasant "turnipy" taste. The *turbidity* showing the presence of water, or of oils which imperfectly mix—as castor and mineral oils—and the *sediment*, either stearin or dirt, are also to be noted; these should be filtered out through paper before the oil is analyzed.

The *elaidin* test (page 1126) may be applied next, to allow time for the cake to form; it will be followed by the *Maumené* test (page 1126) both being done in duplicate. In making the elaidin test it is advisable to carry on an experiment under the same conditions with a known sample of lard oil. These two tests will show whether the sample under examination is a drying or non-drying oil and when the ingredients of the mixture are determined, the results of the Maumené test can be used for calculating their relative amounts. The *iodine* test can be employed to check this result.

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The saponification test, unless mineral or rosin oil be suspected, need rarely be resorted to; the reason being that it would show practically nothing regarding the nature of the oil. Except in the case of castor (Sapn. No. 181), rape (174), sperm (135) and cocoanut (260), this characteristic is about 193.

Finally, where the importance of the case will warrant, the analyst is advised to prepare a mixture of oils using the proper proportions indicated by the various tests, and subject it to the more rapid tests as the specific gravity, viscosity, Maumené and iodine number. In making out the report of analysis it should be borne in mind that, excepting in the case of the special test, the results of *one* test cannot be relied upon to determine the nature of an oil, but the evidence of all the tests here given should be carefully compared and weighed before rendering a final verdict: in consideration of the fact of the wide variation of the characteristics of the oils, it is futile to report the quantities of oil found in a mixture more closely than 1%.

## PETROLEUM PRODUCTS

### (a) Burning Oils

The tests or determinations to be made are, in the order of their importance, flash, fire, specific gravity, distillation, sulphur, free acid, sulphuric acid, mineral salts and water. In some cases the color is determined.

**Flash Test or Point.** By flash point we understand the lowest temperature to which an oil must be heated, to give off vapors which when mixed with air produce an explosive mixture. The results of this test will vary according to the quantity of air over the surface of the oil, and whether this be moving or still; also according to the distance of the testing flame from the surface of the oil. Furthermore, the size of this testing flame, the length of its time of action, its form and dimensions, and lastly, the manner of heating the oil, will all influence the result.<sup>1</sup>

Any cause producing the rapid evolution of a large amount of petroleum vapor tends to lower the flash point. Barometric changes are, for practical work, negligible, each 5 mm. causing a variation of but 0.1° C.

**Determination by the "New York State Board of Health Tester."** The apparatus, Fig. 86, consists of a copper oil cup, *D*, holding about 10 oz., the quantity usually contained in lamps, heated in a water bath by a small Bunsen flame. The cup is provided with a glass cover, *C*, carrying a thermometer, *B*, and a hole for the insertion of the testing flame—a small gas flame one-quarter of an inch in length.

**Manipulation.** After describing the apparatus minutely, the regulations of

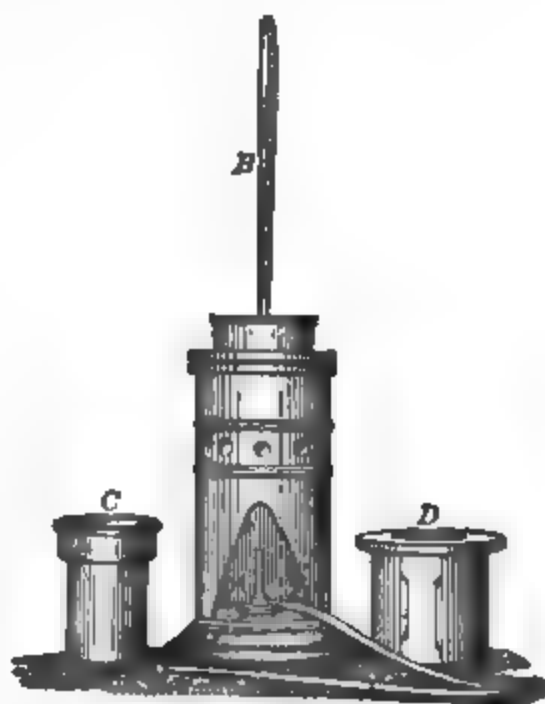


FIG. 86.—N. Y. Tester.

<sup>1</sup> Engler and Haase, Z. Anal. Chem., 20, 3, 1881.

the New York State Board of Health say,<sup>1</sup> "(2) The test shall be applied according to the following directions:

"Remove the oil cup and fill the water bath with cold water up to the mark on the inside. Replace the oil cup and pour in enough oil to fill it to within one-eighth of an inch of the flange joining the cup and the vapor-chamber above. Care must be taken that the oil does not flow over the flange. Remove all air-bubbles with a piece of dry paper. Place the glass cover on the oil cup, and so adjust the thermometer that its bulb shall be just covered by the oil.

"If an alcohol lamp be employed for heating the water bath, the wick should be carefully trimmed and adjusted to a small flame. A small Bunsen burner may be used in place of the lamp. The rate of heating should be about two degrees per minute, and in no case exceed three degrees.

"As a flash torch, a small gas jet one-quarter of an inch in length should be employed. When gas is not at hand employ a piece of waxed linen twine. The flame in this case, however, should be small.

"When the temperature of the oil has reached 85° F. the testings should commence. To this end insert the torch into the opening in the cover, passing it in at such an angle as to well clear the cover, and to a distance about half-way between the oil and the cover. The motion should be steady and uniform, rapid and without any pause. This should be repeated at every two degrees' rise of the thermometer until the temperature has reached 95°, when the lamp should be removed and the testings should be made for each degree of temperature until 100° is reached. After this the lamp may be replaced if necessary and the testings continued for each two degrees.

"The appearance of a slight bluish flame which passes over the entire surface shows that the flashing-point has been reached.

"In every case note the temperature of the oil before introducing the torch. The flame of the torch must not come in contact with the oil.

"The water bath should be filled with cold water for each separate test, and the oil from a previous test carefully wiped from the oil cup."

For the determination with the open tester (Tagliabue's small) reference may be had to the author's "Short Handbook of Oil Analysis"; for the test with the closed tester, Abel's or Abel-Pensky, or Holde's "Examination of Hydrocarbon Oils" translated by Mueller.

**Fire Test.** The fire test of an oil is the lowest temperature at which it will give off vapors which when ignited will burn *continuously*. It is made by continuing to heat the oil (the cover being removed in the case of a closed tester without slipping out the thermometer) at the same rate after the flash test is made and noting the point as indicated above. The flame is extinguished by a piece of asbestos board and the heating discontinued. In the case of many illuminating oils this point is from 10° to 20° F. higher than the flash point.

In the case of "Mineral Sperm" (300° F. fire test oil) these tests should be made with the instrument for lubricating oils (page 1119). The heating should be at the rate of 10° F. per minute, and the testing flame first applied at 230° F. and then every seven degrees until the flashing-point is reached.

The most satisfactory way of making these tests is to place the watch upon the desk and read the thermometer at the expiration of every minute, noting down each reading in the proper column in the laboratory note-book.

<sup>1</sup> Report of the New York State Board of Health, 1882, p. 495.

**Specific Gravity:** (a) *By the Hydrometer.* A hydrometer jar is four-fifths filled with the oil, a verified Baumé hydrometer introduced into it, and the depth read off to which the instrument sinks into the oil. This may be effected by placing a strip of white paper back of the jar and noting the point at which the lower meniscus of the oil touches the scale. The temperature of the oil is taken at the same time, and in case it be not 60° F. (15.5° C.), subtract 1° Baumé from the hydrometer reading, for every 10° F. it is higher than 60°, and add 1° Baumé for every 10° F. it is lower than 60° F. In practice this can be done by Tagliabue's "Manual for Inspectors of Coal Oil," which gives the readings at 60° F. for any gravity from 20° to 100° Baumé, between 20° and 109° F. The specific gravity may be found by the formula<sup>1</sup>  $\frac{140}{130+B}$ , B° representing the reading Baumé at 15.5° C.

(b) *By the Westphal Balance.* This is a specially constructed instrument, Fig. 87, with a glass plummet carrying a thermometer counterbalanced by a weight. Upon immersing the plummet in a liquid the positions of the weights, which must be added to restore the equilibrium, represent the specific gravity directly. The largest weight represents the first decimal place, the next the second, and so on. The instrument is placed upon a level table, and by means of the leveling screw is brought into adjustment—i.e., so that the point upon the beam is exactly opposite the point upon the fixed part.

The plummet is now placed in the vial or balance jar containing the oil, cooled to 15.5° C., hung upon the balance, being careful completely to immerse it in the oil, weights added to restore the equilibrium, and the specific gravity read off as above described.

Care should be taken that the plummet does not touch the sides of the jar or vial. For solid fats and some oils the specific gravity is taken at 100° C., using a special plummet.

**Distillation Test: Engler's Method.** Engler uses a special boiling flask, 6.5 cm. in diameter, with neck 15 cm. long, and with the side tube about 9 cm. from the springing of the bulb; this is connected with a Liebig condenser and heated by a small lamp with a shield.

One hundred cubic centimeters of the oil are measured into the boiling flask and distilled at the rate of 2 to 2.5 cc. per minute, the distillate being caught in a 25-cc. burette or graduate. When the distillation is to be broken, the lamp should be taken away and the temperature allowed to sink 20° and again brought to the breaking or fractionating point, as long as any considerable quantity goes over. The distillation is first broken at 150° C., and then each 50° until 290° C.

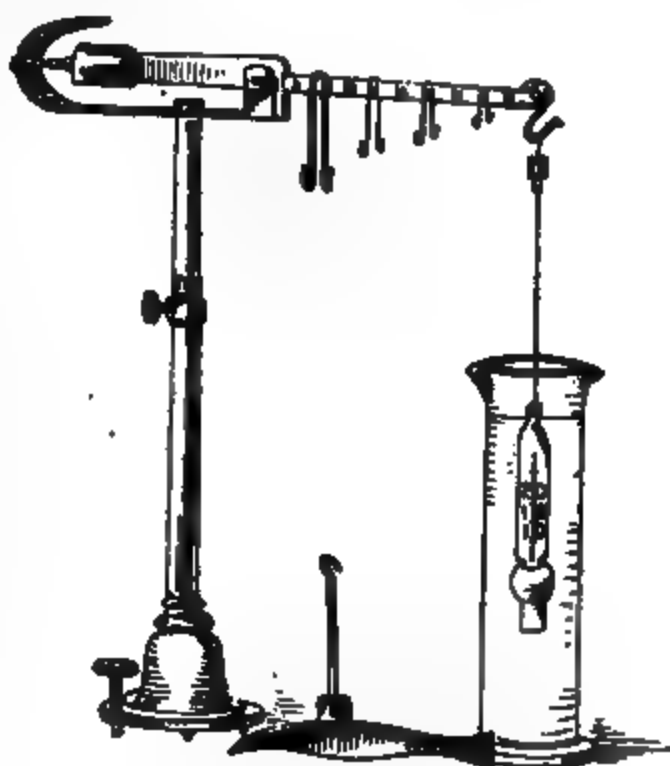


FIG. 87.—Westphal Balance.

<sup>1</sup> This formula applies to liquids lighter than water.

is reached; in this way a much better idea of the value of the oil is obtained than if the distillation were allowed to proceed continuously between these points. The lighter portions, for example, those between 150 and 200°, burn much better than those between 250 and 290°; the heavy portions of American petroleum burn much better than those of the Russian oils.

The averages from four samples of Caucasian and ten samples of American oils subjected to this test were as follows, in per cent by volume:<sup>1</sup>

	Below 150° C.	150-290°	Above 290° C.
Caucasian petroleum.....	8.0	86.6	5.4
American petroleum.....	16.9	57.1	26.0

**Determination of Sulphur.**<sup>2</sup> The deleterious effect of the oxides of sulphur upon hangings and bindings—as well as upon the human system—is well known, sulphuric acid being their ultimate product. The sulphur exists in combination, partly as compounds formed from the sulphuric acid used in refining and partly as alkyl sulphides. Its qualitative detection may be effected by heating the oil to its boiling-point with a bright piece of sodium or potassium. If sulphur compounds be present, a yellowish layer is formed upon the metal. After cooling add distilled water drop by drop until the metal is dissolved, and test for sulphides with sodium nitroprusside.

For the quantitative determination of sulphur 1 to 1½ grams of the oil are burned in a calorimetric bomb containing 10 cc. of water and oxygen under a pressure of 30 atmospheres. A lower pressure sometimes gives inaccurate results. If the sample contains more than 3% sulphur, the bomb is allowed to stand in its water bath for fifteen minutes after ignition of the charge. The bomb is allowed to cool fifteen minutes, opened, and its contents washed into a beaker. If the bomb has a lead washer, 5 cc. of a saturated solution of sodium carbonate is added, the contents are heated to the boiling-point, boiled for ten minutes and filtered. This is necessary to decompose any lead sulphate from the washer. The united washings are filtered and neutralized with HCl, using methyl orange as an indicator. The neutralized solution is poured into the tube of the Jackson turbidimeter,<sup>3</sup> diluted to near the 100-cc. mark, shaken, then acidified with 1 cc. of 1:1 hydrochloric acid, made up to the mark and mixed well by shaking. One of the barium chloride tablets is then dropped in<sup>4</sup> and the tube closed by a clean rubber stopper. The tube is then tilted up and down, causing the tablet to roll back and forth through the solution by gravity. When the precipitation appears to be complete, the remainder of the tablet may be dissolved by rapidly rotating the tube; violent shaking should be avoided. The turbid liquid is transferred to a beaker, the candle lighted, a small quantity of the liquid poured into the glass tube to prevent overheating and cracking, and the tube put in place. More of the liquid is then poured in, allowing it to run down the side of the tube, rapidly at first, until the image of the flame becomes dim, then more slowly, waiting a minute after each addi-

<sup>1</sup> Veith, "Das Erdoel," p. 244.

<sup>2</sup> Allen and Robertson, Technical Paper 26, Bureau of Mines; Chem. Abstracts, 6, 2997, 1912.

<sup>3</sup> Muer, J. Ind. and Eng. Chem., 3, 556, 1911.

<sup>4</sup> From the Frazer Tablet Co., Brooklyn, N. Y.; or 1 gram of barium chloride in dilute solution can be slowly added.

tion until the liquid in the tube is quiet, and continuing thus until the image of the flame just disappears. The depth of the liquid in centimeters is noted and the weight of sulphur found from the table on pages 1220 and 1221. The mixture is returned to the beaker, poured back and forth from beaker to tube two or three times and read again as before.

Or the barium sulphate can be determined in the usual way gravimetrically. In case a turbidity too low to be read with the apparatus be obtained, a larger quantity of oil must be used. Gasolines and light oils can be weighed out in a gelatin capsule.

The percentage of sulphur in a kerosene should not exceed 0.05; the Pennsylvania oils contain usually 0.02 to 0.03, the Lima 0.04 to 0.05.<sup>1</sup>

**Detection of Acidity.** Shake equal quantities of oil and warm water in a test-tube, pour off the oil, and test the water with litmus paper. If the water be strongly acid, the quantity may be determined as in "Free Acid," page 596.

The acid in this case is most probably sulphuric, coming from the refining process.

**Sulphuric Acid Test.** The object of this test is to judge of the degree of refinement of the oil, a perfectly refined oil giving little or no color when submitted to the process. One hundred grams of oil and 40 grams of sulphuric acid, 1.73 specific gravity, are shaken together for two minutes in a glass-stoppered bottle and the color of the acid noticed. For comparative work this color is matched by solutions of Bismarck brown.<sup>2</sup>

**Mineral Salts.** Salts of calcium or magnesium when dissolved in the oil diminish its illuminating power; their action is to form a crust on the wick and prevent access of air.

Redwood<sup>3</sup> states that 0.02 gram of either of these salts in 1000 grams of oil diminishes the illuminating power 30 to 40% in eight hours.

They are determined by distilling 100 to 200 cc. of the oil down to about 20 cc., evaporating and igniting this residue, and subsequently treating with hydrochloric acid. The calcium and magnesium are then determined in the usual way.

**Determination of Water.** By rubbing the oil together with a little eosin on a glass plate the oil will take on a pink color if water be present.

The evaporation method is approximate and applicable only to heavy oils and greases. Its accuracy even with heavy greases is questionable.

Dilute<sup>4</sup> the oil with an equal volume of benzol, whirl it vigorously in a centrifuge until the separated layer of water does not appear to increase in volume. However, as water is somewhat soluble in any diluent used and also in oils, a portion of the water content will fail to appear, consequently the method in which a diluent is used cannot be considered accurate. It is advisable first to agitate the diluent vigorously with water and then to separate with the centrifuge in order to saturate it with water before using.

Groschuff<sup>5</sup> states that 100 grams of benzene will dissolve 0.03 gram of water at 3° C. and 0.337 gram of water at 77° C., whereas petroleum products (density 0.792) will dissolve from 0.0012 gram at 2° C. to 0.097 gram at 94° C.

<sup>1</sup>Kiesel, Ch., *Rev. Fett und Harz. Ind.*, 14, 157, 1906.

<sup>2</sup>J. Soc. Chem. Ind., 15, 678, 1896.

<sup>3</sup>Dingler, *Pol. J.*, 255, 427, 1887.

<sup>4</sup>Reported by Allen and Jacobs. Bureau of Mines Technical Paper No. 25, 1912.

<sup>5</sup>Groschuff, E., "The Solubility of Water in Benzene, Petroleum and Paraffin in Oil," *Chem. Abs.*, 5, 2550, 1911.



While water to the extent even of 3 or 4% is apparently without influence on the viscosity, 1% extinguishes the flame when making the flash test.

**Color.** This test has lost its importance since oils are sometimes satisfactory despite their yellow color. The determination is usually made with the Stammer colorimeter in which the depth of the oil is changed in a cylinder until it matches the color of a standard plate of uranium glass. Standard white oil requires a depth of 50 mm. and water white from 300–320 mm. to match the color of the plate.

For a cut of the instrument and method of using, reference may be had to Holde's "Examination of Hydrocarbon Oils," translated by Mueller, page 52.

### (b) Lubricating Oils

The tests to be made are, in the order of their importance, viscosity, specific gravity, evaporation, cold test, flash test, fire test, test for soap, carbon residue test, friction test. Saponification value, tarry matter insoluble in 88° naphtha, and added impurities are also determined.

The office of a lubricant is to prevent the attrition of axle and journal box by interposing itself between them in a thin layer, upon which the shaft revolves. The ideal lubricant is that which has the greatest adhesion to surfaces and the least cohesion among its own particles, or, as the practical man expresses it, the most fluid oil that will do the work and stay in place. The determination of its viscosity or "body" is then of the first importance.

**Viscosity** is the degree of fluidity of an oil or its internal friction. It is independent of the specific gravity of the oil, although this in the pipette instruments influences the time of efflux. Within certain limits it may be taken as a measure of the value of oil as a lubricant, by comparing the viscosity of the oil under examination with that of other oils which have been found to yield good results in practice.

The instruments employed for its determination may be divided into two classes—pipette viscosimeters, giving the time of efflux, as those of Engler, Saybolt, and others, and torsion viscosimeters, giving the retardation due to the oil, those of Macmichael and Doolittle.

In expressing viscosity, consequently, it is necessary to give the name of the instrument with which it is determined. It is sometimes expressed as specific viscosity, that is, the time of the oil divided by the time of water; this is only comparative when done with instruments of the same name, that is, specific viscosity Engler is not the same figure as specific viscosity Saybolt. Besides this manner of expressing viscosity, it is occasionally measured in absolute (C.G.S.) units or dynes. This is possible when the diameter of the orifice, its length, the quantity and specific gravity of the oil, its time of efflux and change of head are known. Where it is impracticable to determine all these data, by direct measurements, the readings of a viscosimeter may be changed into dynes by determining the viscosity in seconds of standard solutions of glycerine, the viscosity of these being determined in dynes from tables of physical constants. Or it may be done by use of the tables on pages 1117 and 1151.

**Engler Apparatus.** *Description.* The apparatus (Fig. 18) consists of a flat, brass cylindrical vessel, *A*, 106 mm. in diameter and about 62 mm. deep, holding 240 cc., provided with a jet 2.9 mm. in diameter and 20 mm. long. This vessel is gilt inside and the jet, in the standard instruments, is of platinum—ordinarily it is made of brass; the vessel is surrounded with a bath, *B*, either of water or

oil, provided with a stirrer and heated by a ring burner. The jet is closed by the wooden valve, *F*, passing through the cover, and a thermometer, *c*, shows the temperature of the oil; three studs show the height to which *A* is filled and at the same time when it is level. The oil ordinarily is discharged into the 200-cc. flask, although in case the oil or time be limited, 100 or 50 cc. may be used and the time of efflux multiplied by a suitable factor. The instrument is standardized with water, 200 cc. of which at 20° C. should run out in from 50 to 52 seconds.

**Manipulation.** The instrument is thoroughly cleaned with alcohol and ether if necessary and dried; any suspended matter is removed from the oil, which is poured into it up to the level of the studs, stirred until 20° C. is reached and the bath adjusted to the same temperature. The flask is placed beneath the orifice, the plug raised and the time required for 200 cc. of oil to flow out is noted; this is divided by the water value of the instrument and gives then relative or specific viscosity. If only 50 cc. are allowed to run out the time must be multiplied by 5, and if 100 cc., by 2.35. If only 50 cc. were put in and 40 cc. allowed to run out, multiply this time by 3.62 to obtain the time for 200 cc.; if 66 cc. and 50 cc. run out, multiply by 2.79.<sup>1</sup> If it be desired to express the viscosity in absolute measure (C.G.S. units) it can be done by reference to the table on page 1151. It should be noted that specific viscosity obtained with a different type of instrument, e.g., the Saybolt, is not the same as with the Engler.

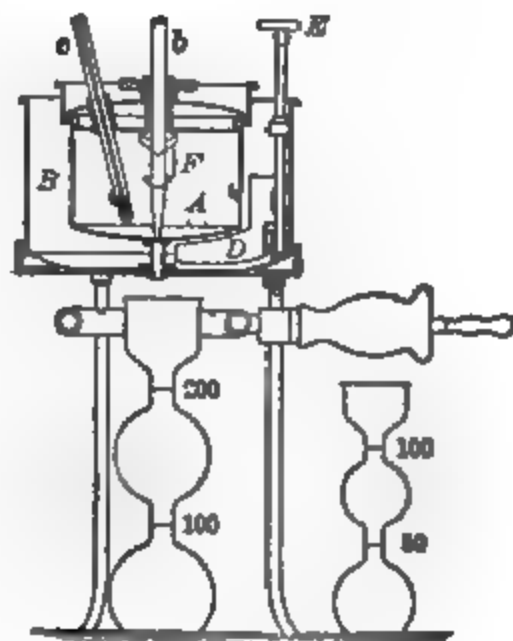


FIG. 88.—Engler Viscosimeter.

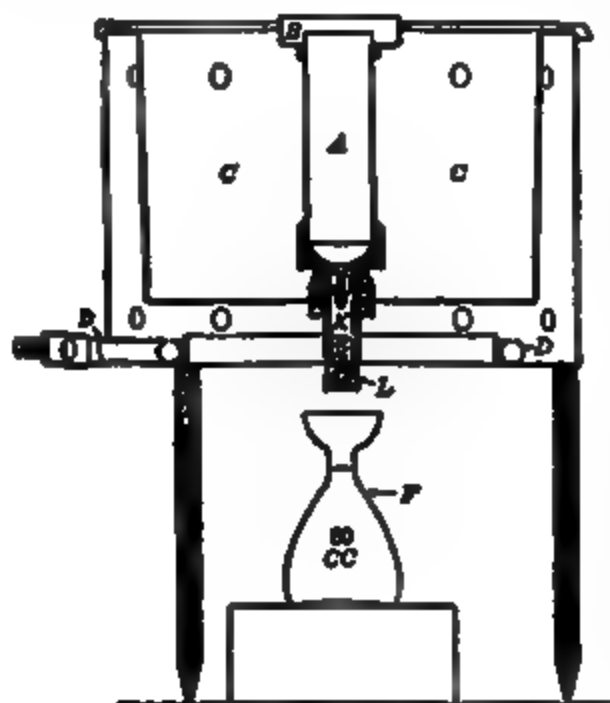


FIG. 89.—Saybolt Viscosimeter.

**The Saybolt Viscosimeter.**<sup>2</sup>—The Standard Universal Viscosimeter is the one now used for testing cylinder, valve, and similar oils at 210° F.; reduced black oils at 130° F.; spindle, paraffin, red, and other distilled oils at 100° F.

**The Universal Viscosimeter. Description.** This consists of a brass tube, *A*, forming the body of the pipette provided with a jet, *K*. The upper part of the pipette is surrounded with a gallery, *B*, which enables a workman to fill it to

<sup>1</sup>Gans, Chem. Revue der Fett und Harz. Ind., 6, 221, 1899.

<sup>2</sup>Redwood, J. Soc. Chem. Ind., 5, 124, 1886. This was formerly made in three forms, A, B, C. Apparatus "A" was the standard for testing at 70° F. Atlantic Red, Paraffin, and other distilled oils; "B" for testing at 70° F. Black Oils of 0°, 15°, 25°, and 30°, Cold Test, and other reduced oils up to, but not including, Summer Cold Test Oil. Apparatus "C" was used for testing at 212° F. Reduced, Summer, Cylinder, Filtered Cylinder, XXX Valve, 26.5° Bé., and other heavy oils.

the same point every time. The pipette is contained in a water bath, *C*, which can either be heated by steam or a ring burner, *D*; a tin cup with spout, a strainer, thermometer, pipette with rubber bulb, stop watch, and beaker for waste oil complete the outfit. It may be used for testing cylinder, valve, and similar oils with bath at 212° and oil at 210°; for testing reduced, black oils, bath and oil at 130°; for testing spindle, paraffin, red and other distilled oil bath and oil at 100°. When used for testing at 212° F., it may be used with either gas or steam alone or both in combination. If with both, the steam may be introduced slowly, more for its condensation to replace evaporation than for real heating purposes, depending upon the gas flame to reach the boiling-point, and keeping it there during the operation of test. The bath vessel should always be kept full during a test, whether at 212°, 130°, or 100°. When used at 130° or 100°, gas alone is used to bring the bath to the prescribed temperature, and turned off during the operation of test, the large size of the bath usually permitting making one test without reheating.

Its dimensions are as follows:<sup>1</sup>

Diameter of overflow cup.....	51 0 mm.
Depth of overflow cup.....	13.0 mm.
Diameter of pipette <i>A</i> .....	30 0 mm.
Depth from starting head to outlet jet.....	113 0 mm.
Length of outlet jet.....	13 0 mm.
Diameter of outlet jet.....	1.8 mm.
Capacity of pipette <i>A</i> .....	70 cc.

*Manipulation.* 1. Have the bath of water prepared at the prescribed temperature.

2. Have the oil strained into one of the tin cups, in which cup it may be heated up to about the standard temperature.

3. Clean out the tube with some of the oil to be tested by using the plunger sent with the instrument.

4. Place the cork (as little distance as possible) into the lower outlet coupling tube just enough to make air-tight, but not far enough to nearly touch the small outlet jet of the tube proper (one-eighth to one-quarter of an inch may be enough).

5. Pour the oil from the tin cup (again through the strainer) into the tube proper until it overflows into the overflow cup up to and above the upper edge of tube proper.

6. Now again see that the bath is at the prescribed temperature.

7. Use the thermometer sent with the instrument by stirring to bring the oil just to the standard temperature.

8. Remove the thermometer.

9. Draw from the overflow cup, with a pipette, all the surplus oil down to and below the upper edge of tube proper. This insures a positive starting head.

10. Place the 60-cc. flask under and directly in line with the outlet jet, and as close to the coupling tube as is practicable to permit of room for drawing the cork.

11. With the watch in left hand draw the cork with the right, and simultaneously start the watch.

12. The time required in the delivery of 60 cc. is the viscosity.

13. Clean out the tube proper before each test with some of the oil to be tested.

14. No drill or other instrument should ever be used in the small outlet jet of tube proper.

<sup>1</sup> Private communication.

The tube should be cleaned out before each test with some of the oil to be tested. Black oils or any oil containing sediment should be carefully strained before testing or "running," as it is technically termed. The instruments should be carefully guarded from dust when not in use.

The results obtained with this instrument are not the same in many cases as those furnished by the A, B, and C instruments, but they seem to have been adopted by the trade generally.

It is worth noting that 3 or 4% of water are apparently without influence on the viscosity.

**MacMichael's Viscosimeter.** This is an instrument of the torsion type in which a disk is suspended in a cup of fluid, the latter being rotated, and the torsion it produces on the disk noted. The disk is suspended by a gold-plated, steel wire 10 inches long, held between two grooved pins at the top of the standard. The brass cup is oil jacketed, the oil covering the wires  $\frac{1}{2}$  inch and heated electrically, or it may be cooled by ice or brine. A bent thermometer passing through the cover indicates the temperature, which may be controlled easily within a fraction of a degree. The graduated dial at the top of the disk is rotary and may be easily set to 0°. A dash pot filled with engine oil on the stem of the disk damps the action of the motor. In operating, the instrument is levelled, the cup is filled to the mark with the fluid to be tested (about 100 cc.), the temperature adjusted, the cup rotated and the readings of the dial noted. These are in degrees of angular deflection, 300 to the circumference, and noted as ° M. = 1/1000 poise. Water at 20° should read 10° M. The smallest, or "practical unit" is 1° M.: by changing the decimal point, practical units, absolute units or specific viscosity may be obtained at one reading of the dial, no calculations being required. Three strengths of wire are supplied, giving water readings of 1°, 10°, and 100°, covering ranges of viscosity to 5000° M. or 5 poise.

The instrument should be calibrated by solutions of pure granulated sugar dried over sulphuric acid, the absolute viscosity of which is shown below. The accuracy of the instrument is well within 0.5 per cent. The instrument is very rapid, the time required for a reading being very short. It can be applied to colloidal or lumpy solutions or suspensions, as limes, clay, glues, gums, explosives, paints or catsups.

VISCOSITY IN CENTIPOISES OF SUGAR SOLUTIONS<sup>1</sup>

Temp. ° C.	Per cent Sugar by Weight			
	0	20	40	60
0	1.789	3.804	14.77	238
5	1.516	3.154	11.56	156
10	1.306	2.652	9.794	109.8
15	1.141	2.267	7.468	74.6
20	1.005	1.960	6.200	56.5
25	0.894	1.704	5.187	43.86
30	0.802	1.504	4.382	33.78

<sup>1</sup> Bingham & Jackson, Bureau Standards Bulletin, No. 298 (1917).

**Absolute Viscosity.** This expresses viscosity in dynes, that is, the force necessary to produce the acceleration of 1 cc. per second on the mass of a gram. It is independent of the instrument used; Engler numbers can be converted to absolute viscosity by the following factors:

Engler No.	Absolute Viscosity Dynes per Sq.Cm. <sup>1</sup>
1.....	0.01006 X specific gravity
2.....	0.1146 X specific gravity
5.....	0.353 X specific gravity
10.....	0.726 X specific gravity
20.....	1.46 X specific gravity
30.....	2.19 X specific gravity
60.....	4.38 X specific gravity

The Engler numbers of 5 or over are quite nearly proportional to the absolute viscosities.

**Specific Gravity.** See under Burning Oils, page 1111.

**Evaporation Test.<sup>2</sup>** The object of this test is to determine what percentage of an oil—more especially a spindle oil—is volatile when exposed to nearly the same conditions as it is on a bearing.

The oil is exposed upon annular disks of filter-paper  $1\frac{1}{2}$  in. outside diameter, with hole  $\frac{1}{2}$  in. in diameter, which have been standing in a sulphuric acid desiccator for several days, contained in a flat watch-glass.

**Manipulation.** The watch-glass and paper are weighed—to tenths of a milligram—and about 0.2 gram of oil brought upon it by dropping from a rod, and accurately weighed. The watch-glass is now placed in an air bath, the temperature of which remains nearly constant at 60° to 65° C. (140° to 150° F.), and heated for eight hours. It is then cooled and reweighed, the loss being figured in per cent. No oil should be passed which gives an evaporation of more than 4%.

The following table of results upon some spindle oils shows the relation of gravity, flash point, and evaporation:

Gravity.	Flash, °F.	Evaporation.	Gravity.	Flash, °F.	Evaporation.
.....	298	7.0%	.862	352	0.9%
.846	318	4.4%	.866	366	1.7%
.....	348	2.0%	.870	<del>352</del>	0.8%
.852	348	1.0%	.882	364	1.7%
.856	336	1.4%			

<sup>1</sup> Waidner, Proc. Am. Soc. Test. Mat., Pt. I, 293, 1915.

<sup>2</sup> Archbutt, J. Soc. Chem. Ind., 15, 326, 1896.

**Norms.** The temperature employed, 65° C., is approximately that attained by a bearing (in a spinning frame) after running two hours, thus leaving the oil exposed to it for eight hours, assuming a ten-hour day.

The test is important to the insurance underwriter, because it measures the amount of inflammable material sent into the air, and hence the liability to cause or aid conflagrations; it is important to the mill-owner, as it indicates the quantity of oil left upon the bearing, hence serving its purpose.

The test is made upon other oils by heating them six hours in a shallow dish to 100°, 150°, 220, or 300°, sometimes in a draft of air.

**Cold Test.** This may be defined as the temperature at which the oil will just flow.

**Manipulation.** A 4-oz. vial is one-fourth filled with the oil to be examined, a short, rather heavy, thermometer inserted in it, and the whole placed in a freezing mixture. When the oil has become solid throughout, let it stand one hour; the vial is removed, the oil allowed to soften, and thoroughly stirred until it will run from one end of the bottle to the other. The reading of the thermometer is now taken by withdrawing it and wiping off the oil with waste to render the mercury visible.<sup>1</sup>

The chilling-point is the temperature at which flakes or scales begin to form in the liquid, and is determined similarly, by cooling the liquid 5° at a time.

**Freezing Mixtures.** For temperatures above 35° F. use cracked ice and water; between 35 and 0° F. use two parts of ice and one part of salt; and from 0 to -30° F. use three parts of crystallized calcium chloride and two parts of fine ice or snow. A still more convenient means is by the use of solid carbonic acid dissolved in ether, giving -50° F. readily.

The preceding method is open to quite an error from the personal equation of each observer. To obviate this Martens<sup>2</sup> proceeds as follows:

The oil is poured into a U-tube 1 cm. in diameter, 16 cm. high, with 3 cm. between the bends, to a depth of 3 cm.; it is then placed in a freezing mixture, cooled, and connected with a blast at a constant pressure of 3 cm. The temperature at which the oil begins to flow under these conditions is considered as the cold test.

**Flash Point.** Several forms of apparatus for testing the flash point of lubricating oils have been devised: Pensky-Martens's closed tester employing a stirrer is used in Germany. Martens states in a later article that stirring is unnecessary. In this country an open cast-iron or spun brass cup—the Cleveland open cup—1½ in. high by 2½ in. in diameter, heated by a Tirrill burner in an air bath is quite extensively used. Dudley and Pease use an open porcelain dish heated with a Bunsen burner.

The cup, Fig. 90, is filled with oil to about ½ in. from the top and the thermometer is suspended so that the bulb is just immersed in the oil. The oil is heated at the rate of 10° F. a minute by a Bunsen burner with a protecting chimney; as the flash point is approached, a test is made for every rise of 3° by slowly passing the small bead-like test flame across the cup near the thermometer. The oil should flash near the thermometer when the proper point is reached. The fire test is, as a rule, 50° to 80° F. higher than the flash point. As the open-cup tests are easily affected by drafts, they are subject to errors of 5° F. The thermometers used should be compared with a standard

<sup>1</sup> Dudley and Pease, *An. Eng. and R. R. J.*, 69, 332, 1895.

<sup>2</sup> *Mitt. kgl. tech. Versuchstation*; abstr. *J. Soc. Chem. Ind.*, 9, 772, 1890.

and corrected for stem exposure. When this is done it is suggested that ' be added to the reading: thus, "flash 379° F. corr."

**Fire Test.** The cover is supported above the cup, and the heat application of the testing flame continued as in making the flash test.

The method of recording is the same as in the case of the illuminati one column for times and another for temperatures. Holde<sup>1</sup> finds that v

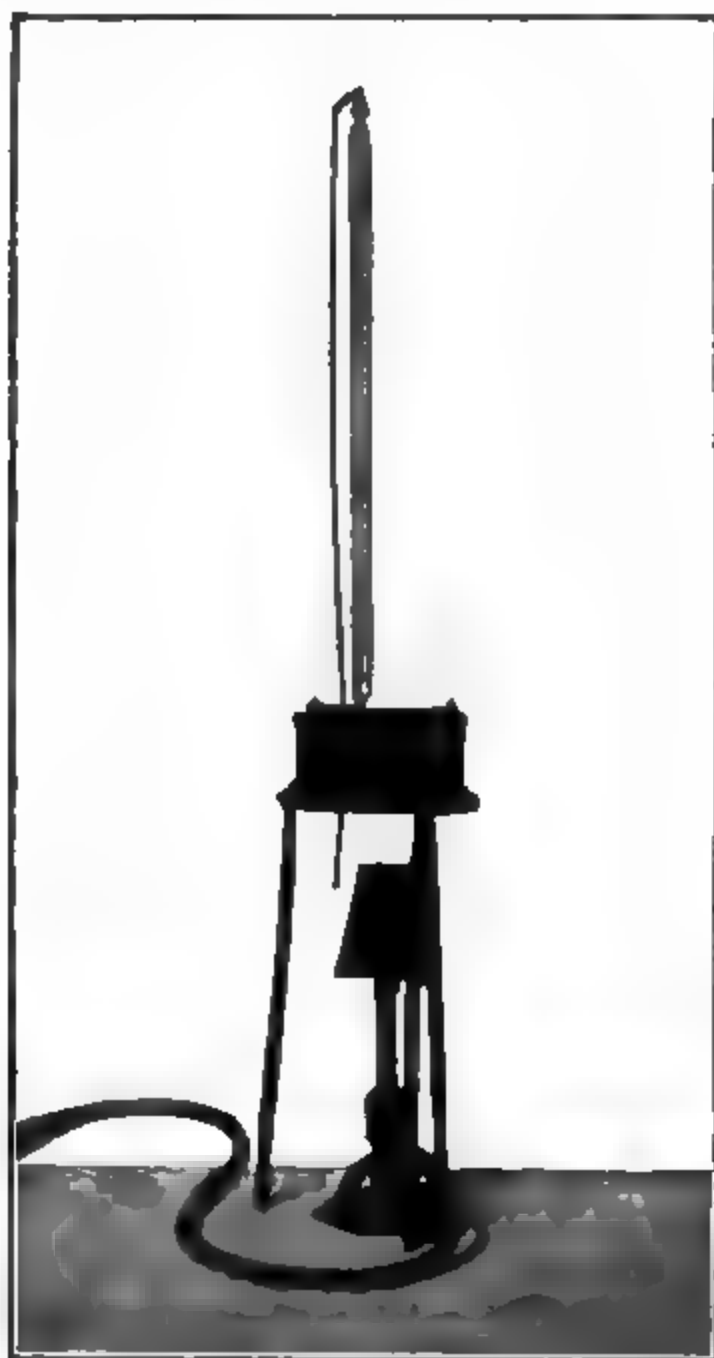


FIG. 90.—Cleveland Cup.

flashing between 172° C. and 241° C. the exact quantity of oil used is of importance. In these particular cases a difference of filling of 13 cc. alters flash point only 1–1.5° C. For the effect of water see page 572.

It is worthy of notice that the free fatty (oleic) acid contained in an oil alters its flash point apparently in proportion to the quantity present.

<sup>1</sup> J. Soc. Chem. Ind., 16, 322, 1897.

**Detection of Soap.** To increase the viscosity of an oil,<sup>1</sup> resort is had to the use of "oil pulp," "oil-thickener," or "white gelatin," usually an oleate of aluminum, though other bases may be present. Its disadvantages are that it causes the oil to chill more easily and to emulsify, thus increasing the friction. Furthermore, it is precipitated by contact with water or steam, causing clogging of the machinery.

The test depends upon the fact that the metaphosphates of the earthy and alkali metals and aluminum are insoluble in absolute alcohol.<sup>2</sup>

The test is applied as follows: five to 10 cc. of the oil to be tested are dissolved in about 5 cc. of 86° gasoline or ether, and about 15 drops of the phosphoric acid solution (Appendix, Reagents) added, shaken and allowed to stand; the formation of a flocculent precipitate indicates the presence of soap. An idea of the kind of soap can be often gained by adding an alcoholic solution of  $\text{PtCl}_4$ . If the precipitate becomes crystalline it is a potash soap; if it dissolves, soda, lime, or magnesia; if unchanged, alumina or iron.

For the accurate determination of these compounds a known weight of the oil must be ignited, the residue determined and quantitatively examined.

**Caoutchouc.** Holde<sup>3</sup> states that 1 to 2% of unvulcanized caoutchouc is sometimes added to oils to increase their viscosity. This may be detected by adding three parts of alcohol to four parts of the ethereal solution, whereby the rubber material is precipitated and may be dried and weighed.

**Test for Fatty Oils.** To detect small quantities of fatty oil ( $\frac{1}{4}$  to 2%) Lux<sup>4</sup> recommends heating a few cubic centimeters of the oil for fifteen minutes with some bits of sodium in a test-tube in an oil bath; a similar test is made with sodium hydrate. The temperature employed should be for light oils about 230°, for dark oils 250°. In case fatty oil be present, the contents of one or both of the tubes solidify to a jelly of greater or less consistence according to the amount of fatty oil present.

The quantitative determination of these oils, as for example in cylinder oils, is effected after the manner of determining the saponification value (p. 1131) or the detection of unsaponifiable oils in fatty oils (page 1132).

Schreiber<sup>5</sup> adopts a method similar to Sweetnam and Henriques, in that he dissolves 5 grams of the oil in 25 cc. of benzole, adds 25–50 cc. N/2 alcoholic potash, and boils for half an hour on the water bath, using a 3-ft. glass tube as a condenser.

**Gumming Test.** This is designed to give an idea of the amount of a change that may be expected in a mineral oil when in use. These resinified products increase the friction of the revolving or rubbing surfaces.<sup>6</sup> It is also a measure of the amount that an oil will "carbonize" in a gas or gasoline engine cylinder. It is applied after the manner of the elaidin test, by thoroughly mixing together 5 grams of the oil in a cordial glass with 11 grams of nitroaul-

<sup>1</sup> In a case which came to the writer's notice the oil would not flow out of the Saybolt "A" apparatus at 70°, at 85° required 1167", and at 110°, 181."

<sup>2</sup> Schweitzer and Lungwitz, *J. Soc. Chem. Ind.*, 13, 1178, 1894.

<sup>3</sup> "Examination of Hydrocarbon Oils," p. 166.

<sup>4</sup> *Z. anal. Chem.*, 24, 357, 1885.

<sup>5</sup> Holde, *Untersuchung d. Schmieröle u. Fette*, p. 175.

<sup>6</sup> *J. Am. Chem. Soc.*, 29, 74, 1907.

<sup>7</sup> Gill, *J. Am. Chem. Soc.*, 24, 467, 1902.

<sup>8</sup> Aisrman, *J. Soc. Chem. Ind.*, 14, 282, 1895.



phuric acid and cooling by immersion in a pan of water at 10–15°. Brownish spots or, in case of a bad oil, masses, form around the edges and become red in the course of two hours. The cordial glass is filled successively three times with 70–86° naphtha and the oil dissolved off the surface of the acid, the gasoline solution being sucked off into a bottle with an air pump. Care is taken not to suck off any of the tarry matter formed. The acid can be neutralized with ammonia and the tar can be collected on a tared filter, washed with gasoline that leaves no residue on evaporation, dried at a low temperature, and weighed as gummy matter. As shown by long practical experience, the oil showing the least tar or gum is the best oil; it also absorbs the least oxygen.

**Carbon Residue Test. Gray's Method.** To a tared 1-oz. quartz flask of the dimensions shown in Fig. 91, add 25 cc. of the oil to be tested and weigh. Wrap the neck of the flask with asbestos paper as far down as the side arm. Stopper tightly with a good cork. Connect to a small aerial condenser by plugging the space with asbestos or glass wool. Provide a shield which will protect the flame and the flask up to the side tube. Using the flame of a good Bunsen or Tirrell burner, heat the flask so that the first drop of distillate will come over in approximately five minutes. Continue the distillation at such a rate that 1 drop per second will fall from the end of the condenser. As the end of the distillation approaches, increase the heat just enough so that no heavy vapors are allowed to condense and drop back into the flask; continue increasing the heat until the flask is enveloped in the flame, and hold the temperature five minutes. Allow the flask to cool, remove the asbestos covering and cork, and burn out completely the carbon and oil in the neck as far down as the side tube, and in the side tube. Heat the bottom of the flask until no more vapors are given off. Cool and weigh.

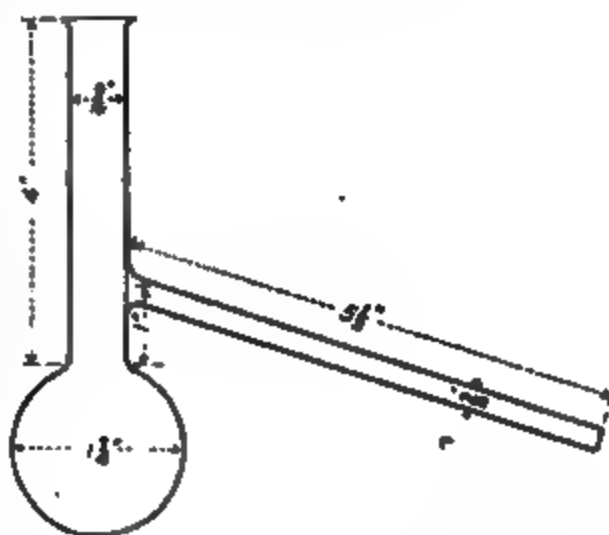


FIG. 91.—Gray's Distillation Flask.

Motor oils, of light and medium grade, range in coke-like residue from 0.06 to 0.5%, the percentage of fixed carbon being roughly proportional to the viscosity of the oil. That is, the higher the viscosity, the higher will be the percentage of fixed carbon, provided the oils have been manufactured from the same grade of crude petroleum by the same general methods. The heavy and extra heavy motor oils range from 0.5 to 1.25%. As the percentage of fixed carbon varies with the viscosities of the oils, the viscosity should be taken into consideration. For illustration, it would not be fair to compare a motor oil having a viscosity of 200 at 100° F., Saybolt, with a motor oil having a viscosity of 400 at the same temperature. The carbon residue in the 200 viscosity oil would be in the neighborhood of 0.2%, whereas the fixed carbon of the higher viscosity oil would be in the neighborhood of 0.75%.

**Gasoline Test.** This shows the presence of tar (still bottoms) or asphaltic matters.

Mix 10 cc. of the oil with 90 cc. 86°–88° gasoline (from Pennsylvania crude); B.pt. 30°–50° C., allow to stand one hour at 70° to 80° F.; not more than 10% of flocculent or tarry matter should have settled out. This settling can be

facilitated by whirling in a centrifuge in a graduated tube in which the volume of the precipitate can be read off. If the test be applied to the oil before making the flash test and then again after this test it shows the extent to which the oil is changed upon heating. Other things being equal the oil which is changed the least is the best oil.<sup>1</sup>

**Microscopical Test.** Put a few drops of the well-mixed oil on a slide and note the nature of the suspended matter—whether carbonaceous specks, flakes of paraffin which disappear on warming, or foreign matter. A good oil should be practically free from all these bodies.

**Heat Test.** Heat 20–25 cc. of the oil in an Erlenmeyer flask or beaker, nearly to the flashing point and keep it at this temperature for fifteen minutes; a satisfactory oil will darken, but remain clear even after standing a day. A poorly refined oil changes to jet black, and forms a carbon-like precipitate. This is usually indicative of an oil that has been refined by acid treatment.

**Herschel's Demulsibility Test.<sup>1</sup>** The test is applicable to non-emulsifying oils, such as are used with high speed engines and turbines, and in its present form does not apply to steam cylinder or other compounded oils. It is made as follows:

Twenty cc. of oil and 40 cc. of distilled water are placed in a 100 cc. cylinder having an inside diameter of 2.6 cm. and heated to 55°. The oil and water are then mixed or emulsified by stirring with a paddle for five minutes at a speed of 1500 R.P.M. The paddle is simply a metal plate 89 by 20 by 1.5 mm. thick, conveniently driven by an electric motor.

The rate at which the oil settles out from the emulsion, when it is allowed to stand at a temperature of 55° is a measure of the emulsibility of the oil. There is a tendency for the rate of settling out of the oil to increase up to a maximum and then decrease, and we may take readings every five minutes (or every minute if the oil separates out rapidly) and note the maximum rate. For example, the following readings were obtained for a certain oil:

Time	Time Since Stopping Paddle	Reading of Cylinder at Top of Emulsion	Cc. of Oil Settled Out	Rate of Settling Cc. per Hour
9.50.....	0	60	0	0
9.55.....	5	57	3	36
10.02.....	12	47	13	65
10.05.....	15	43	19	68
10.10.....	20	41	17	57

The maximum rate is here 68 cc. per hour, and this is called the "demulsibility." The best transformer, motor, and turbine oils settle out in one minute or less, so that if we take readings to even minutes and even cc., the rate would be 1200. Oils are found with rates all the way down from this maximum rate to zero.

It has been found necessary to shake the container holding the sample of oil if it has been allowed to stand for some time, or otherwise the oil poured off from the top may show a different rate of settling from the oil at the bottom. It is also necessary to protect the oil from sunlight which has the effect of decreasing the rate of settling.

<sup>1</sup> U. S. Bureau Standards, Bulletin 86 (1917).

With some oils, under certain conditions, part of the water does not enter into the emulsion and drops of oil adhere to the sides of the cylinder. When this phenomenon occurs, the rate of settling, indicated by the test, is apt to be incorrectly high. The adhering drops may be avoided by using a lower speed or less water, the total quantity of oil and water being kept equal to 60 cc. If part of the water does not enter into the emulsion, but we do not have the above described phenomenon, complete emulsification may sometimes be obtained by prolonging the stirring beyond five minutes, or by increasing the speed.

**Friction Tests.** The writer is inclined to doubt if friction tests are worth the outlay for a machine and the time expended in their execution. Without question they do determine the relative efficiency as regards lubricating power of different oils, but the conditions under which the test is made seldom occur in practice; the bearings upon which the oil is tested are as nearly perfect as can be made, and the feed and load are as regular as is possible; in other words, the conditions are ideal.

The lubricating power of an oil is so closely related to its viscosity<sup>1</sup> that the author believes that results of more practical value can be obtained by the determination of the viscosity of the oils, and subsequent observation of their behavior in actual use than by the longer and more troublesome friction test. Recent experiments,<sup>2</sup> however, have shown that of two oils of the same viscosity and other constants the coefficient of friction of one was 14% less than the other.

In case, however, it be desired to make the friction test, the following machines, it is believed, will be found to be most satisfactory for the purpose:

For spindle oils and light lubricating oils, the machine<sup>3</sup> of the Thurston type which can be run at the highest speed and lowest pressure.

For heavy oils and railroad work, the large machine of the Thurston<sup>4</sup> type, described in his "Friction and Lost Work in Machinery and Millwork," page 254; also in Brannt, page 486; also in Archbutt and Deeley.<sup>5</sup>

## ANIMAL AND VEGETABLE OILS

The tests most commonly employed for the identification of these oils are as follows: specific gravity, refractive index, Valenta test, elaidin test, Maumené test, iodine number, and saponification value.

In addition, certain special and commercial tests are applied, as Bechi test, Baudouin test, free acid, spontaneous combustion, and drying test.

**Specific Gravity.** This is usually determined either by the Westphal balance (page 569) or by the picnometer.

<sup>1</sup> Conradson, J. Ind. and Eng. Ch., 2, 171, 1910.

<sup>2</sup> Brannt, "Petroleum and its Products," p. 510; Woodbury, *vide infra*.

<sup>3</sup> Trans. Am. Soc. Mech. Eng., 32, 834, 1910.

<sup>4</sup> Made by Olsen or Riehle Bros., Philadelphia, Pa.

<sup>5</sup> "Lubrication and Lubricants," 1907, pp. 332-348.

<sup>6</sup> Ibid., p. 359.

<sup>7</sup> Ibid., p. 355.

A two-necked flask of 50 cc. capacity, having a thermometer carefully ground into one neck, the second one being a narrow tube bearing the mark, is most suitable. This is filled with the oil to be examined, cooled to  $15.5^{\circ}\text{C}$ ,<sup>1</sup> the excess of oil removed and weighed. If the weighings be made to 0.5 milligram and a correction applied for the expansion of the glass by the difference in temperature  $= 15.5 - 4 = 11.5^{\circ} = -0.025\%$  of the value obtained, the determination is accurate to 0.00002.<sup>2</sup>

For the determination of the specific gravity of small quantities of oil, satisfactory results can be obtained by weighing 1 or 5 cc. of the oil carefully measured from an accurately calibrated pipette. Or a mixture of alcohol and water can be made until a drop of oil will stay in any position in it, and its specific gravity determined.

**Refractive Index.** This is of the same value as the determination of specific gravity: it has, however, the advantage that it is more rapid and uses only one or two drops of the oil.

The apparatus preferably employed is the Abbé refractometer, Fig. 92, the prisms of which are kept at constant temperature, usually  $25^{\circ}\text{C}$ ., by circulating water.

The illuminating mirror should light the cross hairs and the telescope should be sharply focused on them.

The double prism is opened by means of the screw heads, and after carefully cleansing the prisms with cotton and ether, a drop or two of the oil placed on the horizontal surface of the fixed prism. The prisms are then tightly closed. The telescope is brought into the position shown and the sector is firmly held and the alidade (the moving part) moved forward until the field of vision shows the boundary between light and shade just intersecting the cross hairs.

By means of the screw on the right of the instrument this boundary line should be made as sharp as possible. The index of refraction is read off directly from the sector, using a lens if necessary; the reading is accurate to .0002.

After using, the prisms are again carefully cleansed and a piece of filter paper placed between them to prevent them from being scratched. The instrument is in correct adjustment when water at  $18^{\circ}$  gives a mean reading of 1.333. The temperature correction for oils and fats is 0.0004 for every degree rise.

**Valenta Test.**<sup>3</sup> Although considered by some to be unreliable, yet as the

<sup>1</sup> Allen (Organic Analysis, 33) states that a correction of 0.00064 can be made for each variation of  $1^{\circ}\text{C}$ .

<sup>2</sup> Wright, J. Soc. Chem. Ind., 11, 300, 1892.

<sup>3</sup> Valenta, Dingler polyt. J., 253, 418; also J. Soc. Chem., Ind., 3, 643, 1884.

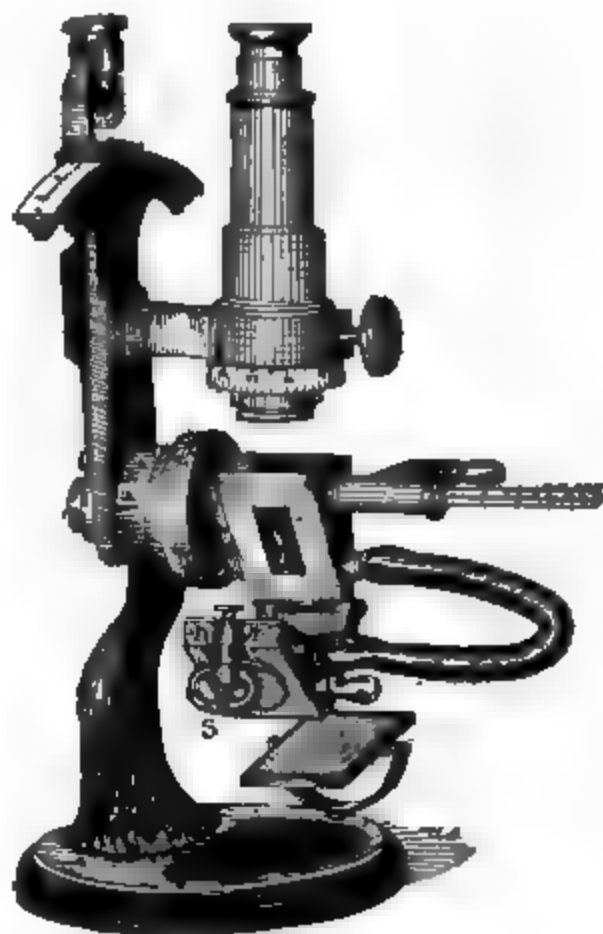


FIG. 92.—Refractometer.

indication given by this test may be of value, it is barely worth the trouble of execution. It depends upon the solubility of the oil in glacial acetic acid.

Enough oil is poured into a test-tube to fill it to the depth of about 1 in., the exact height being marked by the thumb; an equal quantity of glacial acetic acid is poured in, that is, until the acid reaches the point indicated by the thumb. A light thermometer is placed in the tube, and it is heated until the oil dissolves—shown by the liquid becoming homogeneous. The tube is now allowed to cool, and the point noted at which it begins to become thoroughly turbid.

Castor oil is soluble at ordinary temperatures, while rape-seed and other cruciferous oils are usually insoluble even at the boiling-point of the acid. The temperatures at which other oils become turbid are given on pages 1148 and 1149.

**Elaidin Test.** Although this is not a quantitative test, yet its ease of application and the conclusions which may be drawn from it render it valuable. It depends upon the change of the liquid olein into its solid isomer elaidin, and is especially applicable to olive and lard oils.

**Manipulation.** Five grams of the oil are weighed <sup>1</sup>—within 2 drops—into a cordial glass, 7 grams of nitric acid, specific gravity 1.34, are then weighed into it,<sup>1</sup> and two pieces of copper wire (0.6 to 1.0 gram) added. Place the glass in a pan of cold water at about 12° C., and stir with a short glass rod about 20 to 30 turns, not only with a rotary movement, but also with an up-and-down motion, so as to mix the oil and the evolved gas thoroughly. When the wire has dissolved, add a second piece and stir as before. This second addition should furnish gas enough if the liquid has been kept cool and the stirring has been thorough.

At the end of the first hour, pure lard oil will usually show flakes of a wax-like appearance, and upon standing without disturbance and at the same temperature for another hour, the oil will have changed to a solid white cake hard enough to bear several ounces' weight, or admit of lifting the glass and contents by the glass rod.

Most of the fish and seed oils yield a pasty or buttery mass separating from a fluid portion, whereas olive, almond, peanut, lard, sperm and sometimes neat's-foot oil, yield a solid cake.

Instead of using nitric acid and copper, sulphuric acid of 46° Baumé, containing a little nitric acid and saturated at 0° C. with nitric oxide, may be employed.

*A test should always be made at the same time with an oil of undoubted purity.*

**Notes.** If the oil be stirred too much or too frequently, or is too warm, it has no opportunity to form a hard cake.

Hübl states that all attempts to make the test a quantitative one have resulted in failure.

Mercury can be used instead of copper.

Cailletet's method,<sup>2</sup> in which a smaller quantity of oil is used, and sulphuric and nitric acids allowed to act upon it in a boiling water bath, cannot, in the experience of the writer, be depended upon to give reliable results.

**Maumené Test.<sup>3</sup>** While this, like the preceding, is not a quantitative test, yet the indications afforded by it are of more value in many cases than those obtained by quantitative methods, as, for example, the saponification value. It depends upon the heat developed by the mixing of the oil with strong sul-

<sup>1</sup> Not on the analytical balance.

<sup>2</sup> Milliau, J. Am. Chem. Soc., 15, 156, 1893.

<sup>3</sup> SO<sub>2</sub>Cl gives similar results.

phuric acid. This takes place in a small beaker  $7\frac{1}{2}$  to 9 cm. deep and of 150 cc. capacity, packed in an agate-ware cup with dry felt or cotton waste packing.

**Manipulation.** Fifty grams of the oil are weighed <sup>1</sup> into the beaker to within 2 drops, and its temperature noted by a thermometer. Ten cc. of sulphuric acid are now run gradually into the oil—allowing the graduate to drain five seconds—the mixture being stirred at the same time, and the stirring continued until no further increase in temperature is noted. The highest point at which the thermometer remains constant for any appreciable time is observed, and the difference between this and the initial temperature is the “rise of temperature.” This varies with the strength of the acid employed, and to secure uniformity <sup>2</sup> the results should be expressed by dividing the rise of temperature with the oil by the rise of temperature with water, and multiplying by one hundred. This is called the “specific temperature reaction.” The rise of temperature with water is determined in the same manner as with oil, using the same vessel.

**NOTES.** In performing this test it is important that the oil and acid be of the same temperature, attained by keeping them beside each other.

The strength of acid should be as far as possible the same; it should be determined not by specific gravity, but by titration, as 100% and 94.3% acid have the same specific gravity.

For concordant results the conditions should be the same, and the same apparatus should be used. In case the test is to be applied to a drying oil, it should be diluted one-half with a mineral oil, 25° paraffin, for example, thoroughly mixing them. The “rise of temperature” is then, the rise of temperature of mixture minus half the rise of temperature of 50 grams of mineral oil, multiplied by 2.

It is advisable to make a test at the same time with an oil of known purity. Results should agree within 2%. By the use of the Hübl formula, page 1130, substituting thermal values, results comparable with those obtained with the iodine value can be obtained.

Sherman, Dansiger, and Kohnstamm <sup>3</sup> have studied this method with the idea of eliminating the errors. Rather than dilute the oil with a mineral oil they dilute the acid, using one of 89%. The results obtained are a little lower for vegetable oils and a little higher for animal oils than those usually found with the strong acid as employed by Thomson and Ballantyne. Mitchell <sup>4</sup> uses an inert diluent—carbon tetrachloride—in a vacuum-jacketed tube and one-fifth the quantities; all oils are diluted. He finds that the results obtained are in close agreement with the bromine thermal values; further, that the test may be of use in determining the degree of oxidation of fats and oils, the figures becoming greater with the age of the oil.

Data upon various oils will be found on pages 1147–1149.

#### References.

- Maumené, *Compt.-Rend.*, **35**, 572, 1852.  
Ellis, *J. Soc. Chem. Ind.*, **5**, 361, 1886.  
Thomson and Ballantyne, *J. Soc. Chem. Ind.*, **10**, 234, 1891.  
Richmond, *Analyst*, **20**, 58, 1895.  
Mumroe, *Am. Pub. Health Ass'n*, **10**, 236, 1884.

**Iodine Number or Value:** This is the percentage of iodine absorbed by an oil; the method depends upon the fact that different oils absorb different amounts of the halogens; the process is mainly one of addition, although small quantities

<sup>1</sup> Not on the analytical balance.

<sup>2</sup> Tortelli, *J. Soc. Chem. Ind.*, **23**, 668, 1904, is unable to secure uniformity in this way.

<sup>3</sup> *J. Am. Chem. Soc.*, **24**, 266, 1902.

<sup>4</sup> *Analyst*, **26**, 169, 1901.

of substitution products are formed. For example, the unsaturated body olein,  $(C_{17}H_{33}COO)_3C_3H_5$ , when brought in contact with iodine takes up 6 atoms and forms the *addition product*, di-iodo stearin,  $(C_{17}H_{31}I_2COO)_3C_3H_5$ . Palmitin,  $(C_{16}H_{31}COO)_3C_3H_5$ , when similarly treated, forms no addition product, but a small quantity of the *substitution product*, iodo-palmitin,  $(C_{16}H_{29}ICOO)_3C_3H_5$ , and the hydrogen displaced unites with the iodine to form hydriodic acid. The quantity of hydriodic acid thus formed is a measure of the amount of substitution.<sup>1</sup>

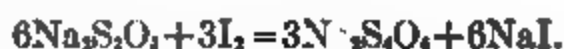
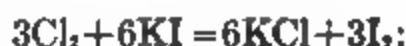
1. *Hanus's Method. Manipulation.* From 0.12 to 0.15 gram of a drying oil, 0.2 to 0.3 gram of a non-drying oil, or 0.6 to 0.7 gram of a solid fat, is accurately weighed into a *d y* 200-cc. bottle. This should be of colorless glass and be provided with a well-ground stopper. This is best effected by pouring out about 5 grams of the oil into a No. 1 beaker containing a short stirring rod, and setting it into a watch-glass upon the pan of the analytical balance. The whole system is weighed, the beaker removed, and several drops of oil transferred to the bottle by dropping down the rod, being careful that no oil touches the neck. Eight drops are approximately 0.2 gram. The beaker is replaced in the watch-glass and the system again weighed, the difference in weight being the amount of oil in the bottle.

The oil is dissolved in 10 cc. of chloroform, 30 cc. of the iodine solution (Reagents) added—best from a burette and allowed to stand with occasional shaking for exactly fifteen minutes; with oils of an iodine number of less than 100, ten minutes suffices; 15 cc. of potassium iodide solution<sup>2</sup> are added and the solution titrated, with or without the addition of starch, with sodium thiosulphate until the halogen disappears.

At the same time at which the oil is prepared, two "blanks" should be prepared similarly in every way to the actual tests, except in the addition of the oil, and treated in every respect like them; the strength of the thiosulphate solution should also be determined the same day on which this test is carried out.

*Standardization of the Thiosulphate Solution.* Ten cc. of potassium iodide and 100 cc. of water are poured into the Erlenmeyer flask; 20 cc. of the bichromate solution, equivalent to 0.2 gram of iodine, are now measured in with a pipette, and to this 5 cc. of strong hydrochloric acid added and the mixture shaken for three minutes. It is now titrated with the thiosulphate solution until the yellow color of the iodine has almost disappeared; starch paste is now added, and the titration continued until the deep-blue color of the solution changes to a sea-green—due to  $CrCl_3$ ,—which is usually brought about by the addition of a single drop.

The reactions involved are:



NOTES. Wijs<sup>3</sup> uses iodine chloride instead of bromide; it is more troublesome to prepare and gives results about 1.2 points higher.<sup>4</sup> Either of these methods has the advantage over Hübl's—first, that the solutions keep better, remaining practically

<sup>1</sup> McIlhenny, J. Am. Chem. Soc., 16, 275, 1894.

<sup>2</sup> This is the original method. Tolman adds here 100 cc. water as in the Hübl method.

<sup>3</sup> Berichte, 31, 752, 1898.

<sup>4</sup> Tolman and Munson, J. Am. Chem. Soc., 25, 244, 1903.



unchanged for several months; secondly, that the action is about sixteen times as rapid, it being completed in fifteen minutes; thirdly, that the solutions are cheaper.

Acetic acid cannot be displaced by carbon tetrachloride as a solvent, as the last traces of iodine are difficult to remove from it. The acetic acid used should be at least 99.5% and show no reduction with potassium bichromate and sulphuric acid.

**2. Hübl's Method. Manipulation.** The oil is weighed out as in 1, into 300-cc. bottles, except that about 25% more may be used.

The oil is now dissolved in 10 cc. of chloroform, 30 cc. of iodine and mercuric chloride solution added, the bottle placed in a dark closet, and allowed to stand, with occasional gentle shaking, for four hours. If the solution becomes nearly decolorized after two hours, an additional quantity should be added. One hundred cc. of distilled water and 20 cc. of potassium iodide are added to the contents, and the excess of iodine titrated with sodium thiosulphate. If at this point a red precipitate ( $HgI_2$ ) is formed, more potassium iodide should be added. As the chloroform dissolves some of the iodine, the titration can proceed until the chloroform layer is nearly colorless, then the starch solution is added, and the operation continued to the disappearance of the blue color.

"Blanks" should be titrated as with the foregoing process, page 1128.

**Notes.** The method was proposed by Cailletet in 1857, made use of by Mills and Snodgrass<sup>1</sup> in 1883, using, however, bromine and carbon bisulphide, and described in almost its present form by Hübl.<sup>2</sup> The chief factors in its execution are (1) strength of the iodine solution; (2) the quantity used; and (3) the length of its time of action:

1. *The Strength of Iodine Solution.* According to Hübl's original memoir, the solutions can be kept indefinitely when mixed.

Fabron<sup>3</sup> states that the solution deteriorated as much as from 17 to 23% in eight days. Ballantyne<sup>4</sup> confirms the deterioration, but finds it much less, 5 to 8% in thirty-eight days. This weakening of the solution is probably due to the hydriodic acid formed by the action of the iodine upon the alcohol.<sup>5</sup>

The mercuric chloride acts apparently as a carrier of iodine, as the reaction takes place very slowly without it (Gantter).<sup>6</sup> Waller<sup>7</sup> finds that the addition of 50 cc.  $HCl$ , specific gravity, 1.19, to the mixed iodine solution preserves it for months. Of the other metallic chlorides,  $CoCl_2$  gives the highest true iodine value,  $MnCl_2$ ,  $MnBr_2$ , and  $NiCl_2$  cause practically no addition. (Schweitzer and Lungwitz.)<sup>8</sup>

2. *The Quantity of Iodine Solution Used.* The mixed iodine solution as made up should require about 53 cc. of the thiosulphate. Before using, a rough titration should be made, and if it be much weaker than this, a proportionately larger amount added. The action of a large excess of iodine is to increase the substitution rather than addition; increase in temperature or in time produces the same effect.<sup>9</sup>

The excess of iodine recommended is from 150 to 250%; some observers recommend from 400<sup>10</sup> to 600%.<sup>11</sup>

3. *Length of Time.* Two hours is sufficient for olive oil, tallow, and lard, while for linseed oil, balsams, and resins twenty-four hours should be allowed.<sup>12</sup>

<sup>1</sup> J. Soc. Chem. Ind., 2, 435, 1883.

<sup>2</sup> Dingler polyt. J., 252, 281; also J. Soc. Chem. Ind., 3, 641, 1884.

<sup>3</sup> J. Chem. Ind., 11, 183, abstr., 1892.

<sup>4</sup> Ibid., 12, 1100, abstr., 1894.

<sup>5</sup> J. Soc. Chem. Ind., 14, 130, 1895.

<sup>6</sup> Ibid., 12, 717, abstr., 1893.

<sup>7</sup> Chem. Ztg., 19, 1786, 1831, 1895.

<sup>8</sup> J. Soc. Chem. Ind., 14, 1031, 1895.

<sup>9</sup> J. Soc. Chem. Ind., 12, 717, abstr., 1893.

<sup>10</sup> Ibid., 14, 1031, 1895.

<sup>11</sup> Holde, Mitt. kgl. Techn. Versuchs., 9, 81, 1891.

<sup>12</sup> Dieterich, J. Soc. Chem. Ind., 12, 381, 1893.



Ingle<sup>1</sup> has shown that the free acid formed during the process is due to the action of water upon the iodochlorides. Some of these are reduced by potassium iodide with liberation of iodine and consequent reduction in the iodine absorption. Iodine chloride is the active agent, and not hypoiodous acid.

For the calculation of the percentage of adulteration of one oil by another, Hübl gives the following formula:<sup>2</sup>

"Let  $x$  = percentage of one oil and  $y$  = percentage of the other oil, further,  $m$  = iodine value of pure oil  $x$ ,  $n$  of pure oil  $y$ , and  $I$  of the sample under examination, then

$$x = \frac{100(I - n)}{m - n} "$$

He further states that the age of the oil, provided it be not rancid or thickened, is without influence on the iodine value. Ballantyne<sup>3</sup> finds that light and air diminish the iodine number.

As might be expected, the iodine value is inversely proportional to the cold test.

The method, as will be seen, is a conventional one, and the best results will be obtained by using measured quantities of reagents and carrying through the process in the same manner every time.<sup>4</sup>

The calculation is perhaps most easily made as follows: Subtract the number of cc. of thiosulphate used for the titration of the oil, from that obtained by titrating the blank—this gives the thiosulphate equivalent to the iodine absorbed by the oil. Multiply this number (of cc.) by the value of the thiosulphate in terms of iodine, and the result is the number of grams of iodine absorbed by the oil; this divided by the weight of oil used and multiplied by 100 gives the iodine number.

In case it be desired to recover the iodine used, reference may be had to an article by Dieterich, abstracted in the Jour. Soc. Chem. Ind., 15, 680, 1896.

**Oxidized Oils. Iodine Number of.** To find the original iodine number of a semi-drying or non-drying oil which has been altered by atmospheric oxidation, add 0.8 to the iodine number found on the altered sample for each increase of 0.001 in the specific gravity (taken at  $\frac{15.5^{\circ}\text{C.}}{15.5^{\circ}\text{C.}}$ ).<sup>5</sup>

**Bromine Number or Value.** The iodine method just described has, among others, the disadvantage that it fails to distinguish between addition and substitution; this is sometimes of importance, and to accomplish it McIlhenny<sup>6</sup> makes use of the bromine absorption.

**Manipulation.** From 0.2 to 0.3 gram of a drying oil, 0.4 to 0.5 of a non-drying oil, or 1.0 to 1.2 grams of a solid fat, are accurately weighed into the 300 cc. bottle, as in the iodine number (page 1128).

The oil is dissolved in 10 cc. of carbon tetrachloride, and 20 cc. of bromine solution (Reagents) added, best from a burette. After allowing it to stand two minutes by the watch, 20 or 30 cc. of potassium iodide are added, in the manner

<sup>1</sup> J. Soc. Chem. Ind., 21, 587, 1902.

<sup>2</sup> Dingler polyt. J., 253, 281, 1884.

<sup>3</sup> J. Soc. Chem. Ind., 10, 31, 1891.

<sup>4</sup> If, for example, the water be added before the iodide solution, the iodine number is changed by 0.3 per cent.

<sup>5</sup> Sherman and Falk., J. Am. Chem. Soc., 27, 608, 1895.

<sup>6</sup> J. Am. Chem. Soc., 21, 1064, 1899.

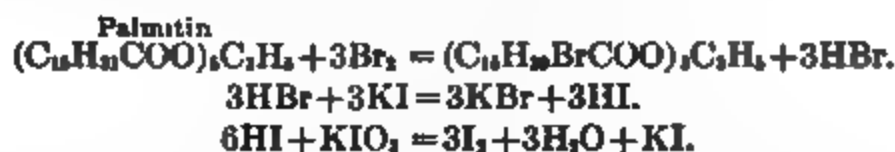
described below, the amount depending upon the excess of bromine. To prevent loss of bromine and hydrobromic acid, a short piece of thin and wide rubber tubing—"bill tie tubing"—is slipped over the lip of the bottle, thus forming a well around the stopper; some of the iodide solution is poured into this and the bottle cooled in cracked ice. Upon removing the stopper the solution is sucked into the bottle, it is shaken to insure the solution of the vapors, and the remainder of the reagent added. The iodine liberated is titrated by sodium thiosulphate in the usual way.

When this titration is finished, 5 cc. of the potassium iodate solution are added and the titration repeated. The iodine liberated in this reaction is equivalent to the hydrobromic acid present. Blank determinations should be made with the reagents used, as with the iodine number.

**Notes.** Oftentimes, particularly with resins, emulsification of the solution takes place, masking the end-point. This can be prevented by the addition of 50 or 100 cc. of a 10% solution of salt.

In case ice be not at hand, the vapors will probably be completely absorbed by passing through the iodine solution in the rubber well.

The reactions involved, in addition to those on page 1128 are:



The calculation is similar to that followed in the iodine number (page 1128).

The percentage of bromine found as hydrobromic acid is called the bromine substitution figure, and the total percentage absorbed, less twice the bromine substitution figure, gives the bromine addition figure.

The method has the further advantages that it is rapid, the bromine solution is permanent and inexpensive. For data upon various oils, see table on page 1147.

**Saponification Value.** This is expressed by the number of milligrams of potassium hydrate necessary to saponify one gram of the oil. It is called from the originator "Koettstorfer<sup>1</sup> number or value," also "Saponification number," and must not be confounded with "Saponification equivalent" as proposed by Allen,<sup>2</sup> which is the number of grams of oil saponified by 56.1 grams of potassium hydrate.

**Manipulation.** One to 2 grams of the oil are weighed out into a 200-cc. Erlenmeyer flask (as in the iodine value, *q. v.*, page 1128) and saponified by 25 cc. N/2 alcoholic potash accurately measured from a burette, by heating upon a water bath, a 1-in. funnel being inserted in the flask.

When the saponification is complete, shown by the homogeneity of the solution, a few drops of phenolphthalein are added and the excess of alkali titrated with N/2 hydrochloric acid. Two blank determinations of the strength of the N/2 potassium hydrate must be made simultaneously, by heating 25 cc. under the same conditions as when mixed with the oil and for the same length of time.

**Notes.** Many prefer to cork the flasks tightly and tie down the stoppers, thus saponifying under pressure; others make use of a return flow condenser, oftentimes merely a long glass tube.

Smetham<sup>3</sup> adds 20 cc. of ether and finds that it aids saponification. Henriques<sup>4</sup>

<sup>1</sup> Z. anal. Chem., 18, 199, 1879.

<sup>2</sup> Commercial Organic Analysis, 2, 40.

<sup>3</sup> Analyst, 18, 193, 1893.

<sup>4</sup> Z. angew. Chemie, 721, 1895.

uses 3 to 4 grams of oil, 25 cc. of petroleum ether, and 25 cc. of normal alcoholic potash, saponifying in the cold by allowing to stand overnight; the advantage consists in preventing the change in the solution by boiling.

McIlhenny<sup>1</sup> has applied the process to dark-colored substances by making use of the principle that when ammonium chloride is added to a neutral soap solution, and the mixture distilled, the amount of ammonia freed is equivalent to the quantity of alkali combined with the fatty acids. As a description of the process is beyond the scope of the present volume, reference must be had to the original article.

As ordinarily prepared, the alcoholic potash solution turns rapidly reddish-brown, so that it is very difficult to note the end-point. This trouble can be partially avoided by adding a drop or two of the solution to the diluted indicator contained upon a tile after the manner of the titration of iron by bichromate. As the color is probably due to the polymerization of the aldehyde formed by the oxidation of the alcohol, it is more satisfactory to use for the preparation of the potash solution an alcohol which is practically aldehyde free. This is best made, according to Dunlap,<sup>2</sup> as follows: 1½ grams of silver nitrate are dissolved in 3 cc. of water, added to 1 liter of alcohol and thoroughly shaken; 3 grams of potassium hydrate are dissolved in 15 cc. of warm alcohol and, after cooling, added to the alcoholic silver nitrate and thoroughly shaken again, best in a tall bottle or cylinder. The silver oxide is allowed to settle, the clear liquid siphoned off and distilled. Alcoholic potash made up from this, using the so-called "potash by alcohol," will give a solution which will remain water-white for weeks.

The writer has found, if the stock solution be kept under an atmosphere of hydrogen, that the coloration by standing is almost entirely prevented.

**Detection of Unsaponifiable Oils.** The qualitative detection takes place by observing the behavior of the solution obtained by boiling the oil with alcoholic potash when diluted with warm water. Any unsaponifiable material will manifest itself as oily drops in the clear alcoholic solution, or as a whitish cloud on the addition of water.

The quantitative determination may take place in two ways: 1. From the saponification number. 2. By gravimetric methods.

1. *From the Saponification Number.* On pages 1148 and 1149 it will be noticed that, except for castor, rape, and sperm oils, the saponification number averages 193. If the number found be divided by this figure, the percentage of saponifiable matter will be obtained; this subtracted from 100 will give the unsaponifiable matter. This method gives no idea of the kind of saponifiable matter.

2. *By Gravimetric Methods.* The procedure is essentially that of Spits and Hönig:<sup>3</sup> 10 grams of the oil are boiled fifteen minutes under a return-flow condenser with 50 cc. of 5% alcoholic potash;<sup>4</sup> 40 cc. of water are added and the boiling repeated. The liquid is allowed to cool, washed into a separatory funnel with 50% alcohol and 50 cc. of 86° gasoline, thoroughly shaken and allowed to stand. The gasoline layer should separate clearly and quickly from the soap solution and the latter is drawn off; the gasoline is washed 2 or 3 times with 50% alcohol to extract any soap, and these washings added to the soap solution. This latter is extracted, until upon evaporation the gasoline leaves no stain upon paper, care being taken to wash the gasoline extracts each time with 50% alcohol; three extractions with gasoline are usually sufficient.

The gasoline is distilled from these extracts, the residue heated until the gas-

<sup>1</sup> J. Am. Chem. Soc., 16, 409, 1894. For a discussion of the theory of the process, see Lewkowitch, J. Soc. Chem. Ind., 17, 1107, 1898.

<sup>2</sup> J. Am. Chem. Soc., 28, 397, 1906.

<sup>3</sup> Z. ang. Chem., 12, 565, 1891.

<sup>4</sup> The potash is made by dissolving purified potash in the smallest possible quantity of water and adding absolute alcohol.

oline odor disappears, and weighed. From the appearance of the residue some idea of the kind of unsaponifiable matter can be obtained. This in the case of sperm oil will be mainly solid alcohols, probably of the ethylene series.

According to Schicht and Halpern<sup>1</sup> this method is open to the following errors: incomplete saponification, incomplete extraction, solubility of soaps in the solvent, and the solubility of the unsaponifiable matter in the washing solution. Their improved method is as follows: 5 grams of fat<sup>2</sup> with 3 of grams solid caustic potash dissolved in a little water and 25 cc. of absolute alcohol are boiled half an hour under a reflux condenser. After cooling 25 cc. of 10% KCl are added and the solution is then shaken four times with 200 cc. of petroleum ether distilling under 60°. The petroleum ether is evaporated and, without washing, the residue is dissolved in 25 cc. absolute alcohol and the solution made slightly alkaline with normal alkali; 25 cc. of 10% KCl are added and the shaking with petroleum ether repeated. The petroleum ether solution is shaken with 100 cc. of 50% alcohol and the wash solution with 100 cc. petroleum of ether, which is afterwards washed with 100 cc. of 50% alcohol. After combining the extracts the petroleum ether is driven off and the residue dried and weighed.

NOTE. Care should be taken to use gasoline which leaves no residue on evaporation at 100° C.

**Identification of the Unsaponifiable Matter.** The unsaponifiable matter is either liquid or solid; in case it is liquid, it may be (1) *hydrocarbon oils*, either mineral, or formed by the distillation of waste fats, as wool grease, or (2) *tar oils*, "dead oils," etc., obtained by the distillation of coal tar; or (3) *rosin oils*.

If it be a question of one of these three, the specific gravity will usually decide it; that of the hydrocarbon oils is 0.855 to 0.930, of the rosin oils 0.96 to 0.99, while the tar oils are heavier than water. Rosin oils would be shown by the Liebermann-Storch test, page 1139; a mixture of mineral and tar oils would be identified by treatment with an equal quantity of nitric acid, sp.gr. 1.45, both previously cooled to 15° C., and noting the rise of temperature. Mineral oils give a very slight rise, being paraffins, while the tar oils belong to the benzole series and are more easily nitrated. Hydrocarbon oils from distilled grease oleins can be identified by their refractive index and rotatory power.<sup>3</sup>

Solid unsaponifiable matters may be:

- (4) *Paraffin*.
- (5) *Ceresene*—refined ozokerite.
- (6) *Higher alcohols* of the paraffin series, as cetyl,  $C_{16}H_{33}OH$ , coming from the saponification of sperm oil and other waxes.
- (7) *Cholesterol*,  $C_{27}H_{48}OH$ , and its isomers, phytosterol, sitosterol, isocholesterol, etc.
- (8) *Lactones*, internal anhydrides of oxy acids as stearylactone,



These may be separated by boiling for two hours with an equal quantity of acetic

<sup>1</sup> Chem. Ztg., 31 279, 1907.

<sup>2</sup> For linseed and other oils, ten or twenty times this weight should be used, the alkali being correspondingly increased.

<sup>3</sup> Gill and Forrest, J. Am. Chem. Soc., 32, 1071; Gill and Mason, J. Am. Chem. Soc., 28, 685.

anhydride; if the substance dissolves and does not precipitate on cooling, higher alcohols are indicated; if a mass of crystals separates out on cooling, cholesterol and its isomers, or a mixture of these with the higher alcohols is indicated; if an oily layer remains on top, it is an indication of the presence of paraffin or cere-sene. For the complete separation and identification of these reference must be had to Lewkowitsch, "Analysis of Fats, Oils, and Waxes," as it is beyond the limits of this chapter.

**Test for Animal or Vegetable Oils.** Animal oils contain cholesterol,  $C_{27}H_{46}OH$ , while vegetable oils contain the isomeric body phytosterol; hence the isolation and identification of these compounds enables one to say with certainty as to the presence of one class of oil or the other—for example as to the presence of fish oil in linseed. The quantity of these bodies varies from 0.2 to 1%. The method is essentially that of Bömer.<sup>1</sup> Fifty grams of the oil are boiled in a flask with a return cooler with 75 cc. of 95% alcohol for five minutes and the alcoholic solution separated; this is repeated with another portion of alcohol. The alcoholic solutions are mixed with 15 cc. of 30% sodium hydroxide and evaporated on a water bath nearly to dryness in a porcelain dish and the residue shaken out with ether. The ether is evaporated, the residue taken up with a little ether, filtered, again evaporated, dissolved in 95% alcohol (by volume), and allowed to crystallize slowly. Bömer states that the form of the crystals is more to be relied upon than a determination of their melting-point. Cholesterol crystallizes from alcohol or ether in leaflets or rhomboid tables containing one molecule of water of crystallization. Phytosterol crystallizes also from alcohol with one molecule of water in needles forming stars or bundles. As a further means of identification, some of the esters should be made and their melting-points determined.

To this end the crystals above obtained are heated over a low flame in a small porcelain dish covered with a watch-glass, with 2 or 3 cc. of acetic or other acid anhydride until it boils: the watch-glass is removed and the excess of anhydride evaporated on the water bath. The contents of the dish are treated with a small quantity of absolute alcohol to prevent crystallization, more alcohol added and the solution allowed to crystallize. The crystals are filtered off through a very small filter, washed with a small quantity of 95% alcohol, dissolved in absolute alcohol, and recrystallized until a constant melting-point is obtained.

The following table shows the corrected melting-points of these alcohols and their esters:

	Cholesterol.	Phytosterol.
Alcohol. ....	148-150.8°	136-143.8°
Acetate. ....	113-114°	120-137°
Benzoate. ....	135-151°	142-148°
Propionate. ....	97-98°	104-105°

**NOTES.** Some directions state, in isolating the cholesterol or phytosterol, to boil with the 30% sodium hydroxide until one-fourth of the alcohol is evaporated. As a result of repeated experiments this has been found to cut down the yield so much that on a large scale practically none of these bodies, particularly phytosterol, was obtained. This agrees with the observation of Lewkowitsch that by heating cholesterol with normal alcoholic potash, cholesterol hydrate is obtained.

The following test will serve to differentiate between cholesterol and phytosterol.<sup>2</sup> A very small quantity of cholesterol is warmed with 1.5 cc. absolute alcohol and a

<sup>1</sup> J. Soc. Chem. Ind., 17, 954, 1898; Tolman, J. Am. Chem. Soc., 27, 590, 1905; Tolman, Bull. 107, U. S. Dept. Agriculture, 1907.

<sup>2</sup> Neuberg and Rauchwerger, abstr. J. Soc. Chem. Ind., 23, 1163, 1904.

ness of isodulcitol or rhamnose ( $\beta$ -dimethylfurfural) added. After cooling, an equal volume of concentrated sulphuric acid is added, so as to form a layer below the solution, whereupon a raspberry-colored ring is produced at the zone of contact of the two liquids. On mixing the layers while the tube is cooled in a current of cold water the mixture becomes intensely colored. With phytosterol the reaction fails or at most a pink color. Similar reactions are given by abietic acid.

As little as 1% of cotton-seed has been found in lard, and 4% in any oil have been detected by this test.

For the means of distinguishing between drying and marine animal oils, see Halphen, *J. Pharm. Chim.*, 14, 391 (1901), abstracted *J. Soc. Chem. Ind.*, 21, 74, or *Chem. Centralb.*, 72, ii, 1097 and 1323.

**Tests for Antifluorescents.**<sup>1</sup> It is often desired to remove the fluorescence or "bloom" from petroleum oils. This may be effected by refining with chromic acid, or more easily by the addition of a small quantity of nitro-naphthalene or nitro-benzene. The latter may often be detected by the odor.

The test is made by boiling about 1 cc. of the oil with 3 cc. of 10% alcoholic potash for one to two minutes. If either of the nitro compounds be present, a blood- or violet-red coloration is produced; a pure mineral oil is changed only to yellow or brownish-yellow by this treatment. In case the characteristic color does not appear the following test may be applied.<sup>2</sup> It depends upon the reduction of the nitro bodies to their amines.

A few cc. of the oil are heated with feathered tin and hydrochloric acid in an Erlenmeyer flask for ten minutes: this can be aided by the introduction of a piece of platinum wire. The oil is separated by a separatory funnel and filtration through a wet filter, the filtrate treated in another separatory with sodium hydrate until the tin hydrate redissolves and shaken out with 10-20 cc. of ether. The amines go into solution in the ether, giving to it a violet color and fluorescence in the case of  $\alpha$ -naphthylamine. These can be recognized by their odor, that of naphthylamine being very characteristic. The latter may be recognized by dissolving in hydrochloric acid, evaporating the latter, and upon treatment with ferric chloride obtaining an azure-blue precipitate. This changes when filtered off to purple-red and the filtrate to violet.

Aniline can be recognized by solution in concentrated sulphuric acid and the red and then blue color which appears on the addition of a small crystal of potassium bichromate. Free aniline is also temporarily colored violet by a solution of bleaching powder.

**Acetyl Value.** The estimation of the acetyl value is seldom required in oil analysis, it being characteristic only when triglycerides are present. For a description of the method and its applications, reference must be had to the larger works, as Lewkowitsch or Allen.

### Special Tests for Certain Oils

Lewkowitsch says: "It should be distinctly understood that color reactions taken by themselves should not be relied upon as giving a decisive answer. At best they can only be used as a preliminary test, or as a confirmatory test. The ease with which this test can be carried out, and its apparent reliability, have led to an over-estimation of this very useful and important reaction; so much

<sup>1</sup> Holde, *J. Soc. Chem. Ind.*, 13, 906, 1893.

<sup>2</sup> Holde, "Examination of Hydrocarbon Oils," p. 168.

<sup>3</sup> "Chemical Technology and Analysis of Fats, Oils and Waxes," 2, 2 3

so, that grave errors may be committed by those who assign to this test an exclusive or even a paramount importance. It is altogether unjustifiable to look upon this test, as has been done, as permitting of quantitative interpretation."

**Bechi's Test for Cotton-seed Oil.** This depends upon the supposition that a substance of an aldehydic nature which reduces silver nitrate is contained in the oil. The method is essentially that of Milliau.<sup>1</sup>

Fifteen grams of oil are weighed into a No. 6 porcelain dish, using the coarse scales, and heated for about ten minutes upon the water bath; a mixture of 10 cc. of 30% caustic soda and 10 cc. of the alcohol is slowly poured upon the oil. The whole is occasionally stirred until the mass becomes clear and homogeneous, and 150 cc. of hot distilled water slowly added so as not to decompose the soap, and the boiling continued until the alcohol is expelled. Dilute sulphuric acid (1:10) is added to acid reaction, and the separated fatty acids washed three times by decantation with cold water. A portion of these is brought into a large test-tube, 15 cc. of alcohol and 2 cc. of 3% silver nitrate solution are added, the tube is wrapped with brown paper, held in place by an elastic band, and heated, with constant stirring, in the water bath until one-third of the alcohol is expelled, which is replaced by 10 cc. of water. This heating is continued for a few minutes longer and the coloration of the insoluble fatty acids observed. The presence of cotton-seed oil in any appreciable proportion causes a mirrorlike precipitate of metallic silver, which blackens the fatty acids of the mixture.

**Notes.** The alcohol should be proved free from aldehyde by a blank test. Unless the mixture in the test-tube be thoroughly stirred while heating, it will "bump" and eject the contents. Other methods of procedure consist in applying the test to the oil itself, often after treatment with dilute caustic soda and nitric acid. (Weason.<sup>2</sup>) The writer had a case in which the oil gave the test while the fatty acids gave no blackening, showing there was something in the oil itself other than cotton-seed oil which reduced the silver nitrate. Students have no difficulty in detecting a 5% adulteration with cotton-seed oil.

Dupont<sup>3</sup> thinks that the reduction of silver nitrate is due rather to sulphur compounds contained in the oil; by passing steam over the oil he obtained a product containing sulphur and the oil still gave the Bechi test. This work has been repeated and confirmed by the author.<sup>4</sup> It is to be noted that while the fatty acids blacken silver nitrate they do not color cadmium, lead, or copper salts, but reduce mercury compounds. No indication of an aldehyde was noted by the fuchsine or ammonia tests. The supposition that the reducing substance is aldehydic in its nature finds support in the fact that if the oil be heated to 240°<sup>5</sup> or be kept for some time<sup>6</sup> it loses this peculiar property.

By purifying the acids by the lead salts Tortelli and Ruggieri<sup>7</sup> are able to detect as little as 10% of heated cotton-seed oil.

It is to be noted that pure lard, tung and olive oil are not infrequently met with which give the test, consequently its indications cannot be considered as conclusive.

**Halphen's Test for Cotton-seed Oil.**<sup>8</sup> This depends upon the observation

<sup>1</sup> J. Am. Chem. Soc., 15, 164, 1893.

<sup>2</sup> J. Am. Chem. Soc., 17, 723, 1895.

<sup>3</sup> Bull. Soc. Chem. (3), 13, 696; J. Soc. Chem. Ind., 14, 811, 1895; also Charabot and March, Bull. Soc. Chim., 21, 252, 1899.

<sup>4</sup> Gill and Dennison, J. Am. Chem. Soc., 24, 397, 1902.

<sup>5</sup> Holde, J. Soc. Chem. Ind., 11, 637, 1892.

<sup>6</sup> Wilson, Chem. News, 59, 99, 1889.

<sup>7</sup> J. Soc. Chem. Ind., 20, 753, 1901.

<sup>8</sup> Halphen, J. Pharm. Chim., 390, 1897.



that this oil contains an unsaturated fatty acid which combines with sulphur, giving a colored compound.<sup>1</sup>

*Procedure.* Ten cc. of the oil or melted fat are heated, in a large test-tube with a long glass condenser tube attached, with an equal volume of amyl alcohol and of carbon bisulphide solution of sulphur (Reagents), at first with frequent agitation, in a steam bath, and then, after the violent boiling has ceased, in a brine bath (105–110°) for forty-five minutes to three hours, according to the quantity of adulterant present, the tube being occasionally removed and shaken. As little as 1% will give a crimson wine coloration in twenty minutes.<sup>2</sup>

*Notes.* If the mixture be heated for too long a time a misleading brownish-red color due to burning is produced. The reaction seems to be peculiar to this oil; it is more sensitive with fresh than old fats, and while, by comparison with a blank,  $\frac{1}{4}$  of 1% is noticeable,  $\frac{1}{2}$  of 1% is easily detected. Cotton-seed oil which has been heated to 250° does not give the test; the oil is then not available as food. Heating to 200° does not interfere with the test.<sup>3</sup>

The test is not given by an oil which has been oxidized with sulphuric acid and potassium permanganate, although such an oil gives the Bechi test.<sup>4</sup> This shows that the two tests are not produced by the same substance. Nor is this test or that of Bechi given by an oil which has been treated with chlorine or sulphurous acid.<sup>5</sup> If treated with the former it is no longer edible; an oil treated with sulphurous acid and washed with alcohol cannot be distinguished from ordinary cotton-seed oil and does not, as already stated, respond to either the Halphen or Bechi test. In this case the test for phytosterol is the only means of determining if it has been added to an animal oil. The test is also given by kapok oil, which is used as an edible oil in China, the East and West Indies, and in Africa; baobab oil also gives it.

Lard from hogs fed on cotton-seed meal shows this reaction strongly, as if it were 25% oil.<sup>6</sup> The butter from cows similarly fed also yields the reaction.<sup>7</sup>

The test may be applied to the soaps or fatty acids, provided they are not too deeply colored.

The amyl alcohol cannot be omitted nor substituted by ethyl alcohol without impairing the delicacy of the test.<sup>8</sup> The compound in the oil cannot be removed by treating with animal charcoal.<sup>9</sup>

**Hexabromide Test for Linseed Oil.** The object of the test is to determine the amount of insoluble bromides of the fatty acids contained in the oil.

Fifteen grams of the oil are saponified by boiling with 15 cc. of potassium hydroxide solution, sp.gr., 1.35, and 15 cc. of alcohol in a flask under a reflux condenser; 300 cc. of warm water are added and the solution distilled with steam until the alcohol is removed. Dilute sulphuric acid is added to excess, the solution heated until the fatty acids are obtained as a clear oily upper layer; this is washed several times with hot distilled water until free from sulphuric acid, using methyl orange as an indicator. This does not react with fatty acids of low molecular weight which being soluble in water may redden litmus. This washing is effected in an atmosphere of inert gas, carbonic acid or hydrogen by stopping the flask with a three-holed stopper, carrying a siphon, an entrance and an exit tube for the gas.

<sup>1</sup> Raikow, Chem. Ztg., 24, 562, 583, 1900.

<sup>2</sup> Oilar, Am. Chem. J., 24, 355; abstr. Anal., 26, 22, 1901.

<sup>3</sup> Fischer and Peyan, Analyst, 20, 131, 1905; Soltsien, Z. öfentl. Chem., 5, 135, 1899; J. Soc. Chem. Ind., 18, 865.

<sup>4</sup> Raikow, loc. cit.

<sup>5</sup> Petkow, Analyst, 22, 123, 1907.

<sup>6</sup> Soltsien, Z. öfentl. Chem., 7, 140, 1901.

<sup>7</sup> Wauters, J. Soc. Chem. Ind., 14, 172, 1900.

<sup>8</sup> Soltsien, loc. cit., 25; Oilar, loc. cit.

<sup>9</sup> Uta, Rev. Fett u. Harz. Ind., 9, 125, 1902.



The acids are siphoned into a small Erlenmeyer flask and in case a few drops of water come over—an equal quantity of alcohol added and dried upon the water bath in a stream of dry inert gas.

In order to test for the presence of unsaponified fat, 3 cc. are dissolved in 15 cc. of 95% (by volume) alcohol, and 15 cc. of aqueous ammonia are added. If an appreciable amount of fat has escaped saponification, the mixture will become turbid (Geitel).

Two grams of mixed fatty acids<sup>1</sup> are dissolved in a flask in 27 cc. of dry ether, cooled down to 10° C., and 0.25 cc. of bromine allowed to run into the solution from a very finely-drawn-out pipette, the time allowed for this being about twenty minutes. The remaining 0.25 cc. of bromine is added somewhat more rapidly, within about ten minutes, the bromination thus occupying about thirty minutes. The authors attach great value to the exact observance of the time. The temperature should never be allowed to rise during bromination above 5°. The flask is corked and allowed to stand for two hours at 0°. The ethereal solution is next decanted through a weighed asbestos or paper filter (Lewkowitsch) and the precipitate is washed with five lots of 5 cc. each of dried and cooled ether. After complete draining, the precipitate is dried for two hours at 80° to 85°, and allowed to cool in a desiccator. The temperature is designedly kept below 100°, as the authors found that the color of the hexabromide becomes somewhat gray if the drying takes place at 100°. The melting-point of the hexabromides was 177°, whereas the melting-point of pure hexabromide has been found to be higher. No doubt the low melting-point is due to the drying having been carried out below 100°.

Nevertheless small traces of retained moisture cannot account for the much larger yield of hexabromide which the authors obtained.

The yields of hexabromide obtained by these authors are as follows:

Fatty Acids	Per cent.	Fatty Acids	Per cent.
Perilla oil.....	64.12	Tung oil.....	nil
Linseed oil, Baltic.....	57.96	Soya bean oil.....	up to 7.78
Linseed oil, Dutch.....	51.73	Poppy seed oil.....	nil
Linseed oil, La Plata.....	51.66	Rape oil.....	6.34
Linseed oil Indian.....	50.50		

**Renard's Test for Peanut Oil.**<sup>2</sup> Tolman<sup>3</sup> has modified this as follows:

Weigh 20 grams of oil into an Erlenmeyer flask. Saponify with alcoholic potash, neutralize exactly with dilute acetic acid, using phenolphthalein as indicator, and wash into a 500-cc. flask containing a boiling mixture of 100 cc. of water and 120 cc. of a 20% lead acetate solution. Boil for a minute and then cool the precipitated soap by immersing the flask in water, occasionally giving it a whirling motion to cause the soap to stick to the sides of the flask. After the flask has cooled, the water and excess of lead can be poured off and the soap washed with cold water and with 99% (by volume) alcohol. Add 200 cc. of ether, cork, and allow to stand for some time until the soap is disintegrated, heat on the water

<sup>1</sup> Eibner and Muggenthaler, *Farben Ztg.*, 1912.

<sup>2</sup> Renard, *Compt. rend.*, 73, 1330, 1871; also Archbutt, *J. Soc. Chem. Ind.*, 17, 1124.

<sup>3</sup> Bull. 107, U. S. Dept. Agriculture, 1907, p. 145.

eth, using a reflux condenser, and boil for about five minutes. In the oils most of the soap will be dissolved, while in lards, which contain much stearin, part will be left undissolved. Cool the ether solution of soap to 15° or 17° C. and let it stand until all the insoluble soaps have crystallized out (about twelve hours).

Filter and thoroughly wash the precipitate with ether. Wash the soaps on the filter back into the flask by means of a stream of hot water acidified with hydrochloric acid. Add an excess of dilute hydrochloric acid, partially fill the flask with hot water, and heat until the fatty acids form a clear oily layer. Fill the flask with hot water, allow the fatty acids to harden and separate from the precipitated lead chloride, wash, drain, repeat washing with hot water, and dissolve the fatty acids in 100 cc. of boiling 90 per cent (by volume) alcohol. Cool to 15° C., shaking thoroughly to aid crystallization.

From 5 to 10 per cent of peanut oil can be detected by this method, as it effects a complete separation of the soluble acids from the insoluble, which interfere with the crystallization of the arachidic acid. Filter, wash the precipitate twice with 10 cc. of 90% (by volume) alcohol, and then with alcohol 70% (by volume). Dissolve off the filter with boiling absolute alcohol, evaporate to dryness in a weighed dish, dry and weigh. Add to this weight 0.0025 gram for each 10 cc. of 90% alcohol used in the crystallization and washing if done at 15° C.; if done at 20° add 0.0045 gram for each 10 cc. The melting-point of arachidic acid thus obtained is between 71° and 72° C. Twenty times the weight of arachidic acid will give the approximate amount of peanut oil present. No examination for adulterants in olive oil is complete without making the test for peanut oil. Arachidic acid has a characteristic structure and can be detected by the microscope.

**Bach's Test for Rapeseed Oil.** According to O. Bach,<sup>1</sup> the acids obtained from rapeseed oil are completely insoluble in David's alcoholic acetic acid, in the proportion of 1 to 15, by volume; those from cottonseed, peanut, sesame, and sunflower oil dissolve on heating. Those from the last oil separate as a granular precipitate at 15°, while from the other three they gelatinize. The acids from olive oil are completely soluble at the ordinary temperature. David's acid is made by mixing 22 cc. of 50% acetic acid (by volume) with 30 cc. of alcohol, sp.gr. 0.817, 92.07% (by weight.)

**NOTE.** The author has found that Bach's observation cannot be implicitly relied upon, as some rapeseed oils yield acids which are soluble in David's mixture.

**Liebermann-Storch Test for Rosin Oil.** One or 2 cc. of the oil are shaken with an equal quantity of acetic anhydride and gently warmed. When cool the acetic anhydride is pipetted off and tested by the addition of 1 drop of concentrated sulphuric acid. A fine violet color is produced in the presence of rosin oil. Tung oil and also cholesterol, which is contained in the animal fats, produce a similar coloration; the latter can be removed by saponifying the oil as completely as possible and shaking out the somewhat dilute soap solution with ether or petroleum ether. The soap solution is then acidified, setting free the fatty acids, and these treated with acetic anhydride as if they were the oil.

**Baudouin's, or Camoin's test for Sesame Oil.** Villavecchia and Fabris<sup>2</sup> apply the test as follows: 0.1 gram sugar is dissolved in 10 cc. of hydrochloric acid

<sup>1</sup> Allen, "Commercial Organic Analysis," 2, pt. 1, 128, 1899.

<sup>2</sup> Z. angew. Chem., 509, 1892; abstr. J. Soc. Chem. Ind., 12, 67; also Kerp, Analyst, 4, 246, 1899.

of specific gravity 1.18 in a test-tube, and 20 grams of the oil to be tested added, the whole thoroughly shaken and allowed to stand. In the presence of 1% of sesamé oil the aqueous liquid will be colored red,<sup>1</sup> due to the action of the furfural formed upon the oil. They state that as olive oils of undoubted purity have shown the reaction in the aqueous layer and not in the oily stratum, the color should be looked for in the latter.

The sugar may be replaced by 0.1 cc. of a 2% solution of furfural and half the quantity of oil used.

Milliau<sup>2</sup> saponifies as in the Bechi test and dries the acids at 105°. Lowkowsch<sup>3</sup> states that this is a needless complication. Da Silva<sup>4</sup> states that this test has given colors with certain Portuguese olive oils; also those of Bari Brindisi and Lecce. Kreis<sup>5</sup> states that the active or color-giving constituent is probably phenolic in its nature. The reaction is given by other substances,<sup>6</sup> as vanillin, oil of cloves, and cinnamon; this should be borne in mind in testing oils which have been extracted from confectionery. Rancid fats prevent the coloration; it can, however, be brought about even in rancid fats by the addition of an equal quantity of cotton-seed oil.<sup>7</sup>

**Free Acid Test.** About 10 grams of oil are weighed (to centigrams) into a 250-cc. Erlenmeyer flask, 60 cc. of neutral alcohol (Reagents) added, the mixture warmed to about 60° C., and titrated with N/6 potassium hydrate, using phenolphthalein, the flask being frequently and thoroughly shaken. The result is conventionally reported in per cent of oleic acid; 1.0 cc. N/6 KOH is equivalent to 0.047 gram oleic acid. Or it can be reported like the saponification number, in milligrams of KOH per gram of oil.

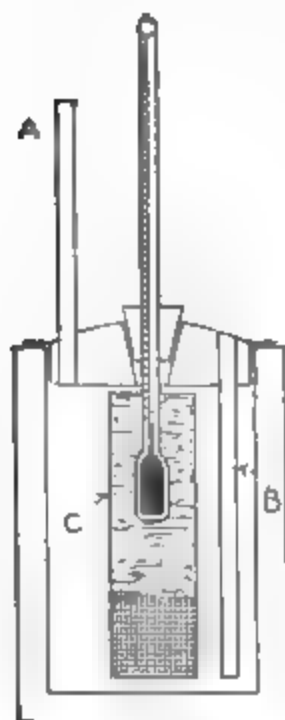


FIG. 92a:

Mackey's Appa-  
ratus.

**Spontaneous Combustion Test. Mackey's Apparatus.** The apparatus,<sup>8</sup> Fig. 92a, consists of a cylindrical copper water bath 7 in. high and 4 in. in diameter (inside measurements), surrounded with a  $\frac{1}{2}$ -in. water-jacket. The cover is packed with asbestos and carries the draft tubes A and B,  $\frac{1}{4}$  in. in diameter and 6 in. long, which cause a current of air to be sucked down B and up A, thus ensuring a circulation of air in the apparatus: C is a cylinder made of 24-mesh wire gauze 6 in. high and 1 $\frac{1}{2}$  in. in diameter and supported upon a projection from the bottom of the bath. A thermometer projects down into the center of the cylinder; if a metal condenser

be connected to the water bath it can be used indefinitely without refilling and without danger of burning out.

Seven grams of ordinary bleached cotton wadding or "absorbent cotton" are weighed out in a porcelain dish or on a watch-glass, and 14 grams of the oil to be tested poured upon the cotton and thoroughly worked into it, care being

<sup>1</sup> Ibid., 1893, 505; abstr. Analyst, 19, 47.

<sup>2</sup> J. Am. Chem. Soc., 15, 162, 1893.

<sup>3</sup> "Oils, Fats and Waxes."

<sup>4</sup> J. Soc. Chem. Ind., 17, 275, 1898.

<sup>5</sup> Chem. Ztg., 27, 316, 1903.

<sup>6</sup> Gerber, Analyst, 32, 90, 1907.

<sup>7</sup> Lauff and Hinsmann, Chem. Ztg., 31, 1023, 1908.

<sup>8</sup> Mackey, J. Soc. Chem. Ind., 15, 90, 1896; Gill, ibid., 26, 185, 1907.

taken to replace any oil that is lost. The cotton is then placed in the cylinder, packed about the thermometer so that it occupies the upper  $4\frac{1}{2}$  in. of the cylinder, and put into the boiling water bath. After the expiration of an hour, the bath having been kept in active ebullition, the temperature is read. Any oil which shows a temperature exceeding  $100^{\circ}\text{C}$ . in one hour, or  $200^{\circ}\text{C}$ . in two hours, should be regarded as a dangerous oil, or liable to produce spontaneous combustion. The following tables show the results obtained in using this apparatus.

Oil.	Temperature $^{\circ}\text{C}$ in		
	1 hr.	$1\frac{1}{2}$ hrs.	$2\frac{1}{2}$ hrs.
Olive (neutral).....	97-98	100	101
Cotton-seed.....	112-128	177-242	194-282
Elaine.....	98-103	101-115	102-191
Olive fatty acids.....	102-114	.....	196

Other values obtained were:

Oil.	Temp. $^{\circ}\text{C}$ .	Time Minutes.	Iodine, No.	Free Acid, per cent.
Olive.....	234	130	85.4	5.3
Lard.....	234	75	75.2	Trace
Oleic acid.....	158	188	60.5	.....
Cotton-seed.....	234	70	108.9	Neutral
Linseed.....	212	65	168.1	Neutral
25° Paraffin.....	57	135	16.2	.....

Besides being used for testing oils it can be applied to testing other materials, oily waste, sawdust, or any mixtures suspected of causing spontaneous combustion.

"The results<sup>1</sup> of the greatest practical value obtained in the use of this apparatus have been, first, determining the cause of fires; and, second, determining the degree of safety of the various oils used in manufacturing. Mineral oil, as is well known, is not liable to spontaneous combustion; and a certain percentage of animal or vegetable oil may be added to mineral oil without materially increasing the danger under ordinary circumstances. This percentage varies according to the oil; with neat's-foot and first quality lard oil some 50 to 60% may be used, with cotton-seed not over 25% is allowable. The claim so often made for so-called 'safe' oils, said to have been changed by special and secret processes of refining so as to be no longer dangerous, is easily exposed by this test."

**Drying Test Upon Glass.**<sup>2</sup> A few drops of oil are brought upon a glass plate inclined at about  $30^{\circ}$  from the horizontal. A test of the oil is made from time to time by touching it with the fingers, the time at which it does not soil them being noted as the point when it is dry. Good oil should dry in three days.

Archbutt<sup>3</sup> makes this test as follows: A piece of polished plate-glass 7 cm. square by 4 mm. thick is cleaned and counterpoised on the balance; it is then heated for an hour at  $200^{\circ}\text{C}$ . in an air bath to thoroughly dry it. It is taken out,

<sup>1</sup> Richards, Tech. Quarterly, 4, 346, 1891.

<sup>2</sup> Amsel, J. Soc. Chem. Ind., 15, 222, 1896.

<sup>3</sup> J. Soc. Chem. Ind., 18, 347, 1899.

laid on a non-conductor, allowed to cool for three or four minutes, and the hot glass thinly painted with the oil to be tested by means of a camel's-hair brush. When the glass is cold it is weighed and sufficient oil added to make it up to 0.1 gram. Two glasses are coated with the sample and two with a standard oil, all placed on a level surface in a large air bath at 50° C. and heated for nine hours; one set of plates is withdrawn, cooled, and tested by the finger. Good raw linseed is tacky, when tested by the finger when cold, in nine hours and dry in twelve; corn oil is practically dry in fifteen hours, though slightly tacky; cottonseed, partially dry in eighteen hours and fully dry in twenty-one. Refined rape oil dried in forty-eight hours, and olive oil was sticky after thirteen days.

**Titer Test.** Under this rather misleading title is expressed the solidification point of the fatty acids derived from a fat or oil; it has nothing at all to do with titration, as might be expected. The test is extensively used for the evaluation of fats, and according to the method provisionally adopted by the Association of Official Agricultural Chemists is carried out as follows:<sup>1</sup>

(a) *Standard Thermometer.* The thermometer must be graduated in tenth degrees from 10° to 60°, with a zero mark, and have an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be at least 1 cm. below the 10° mark, the 10° mark to be about 3 or 4 cm. above the bulb, the length of the thermometer being about 15 in. over all. The thermometer is annealed for 75 hours at 450° C., and the bulb is of Jena normal 16''' glass, moderately thin, so that the thermometer will be quick acting. The bulb is about 3 cm. long and 6 mm. in diameter. The stem of the thermometer is 6 mm. in diameter and made of the best thermometer tubing, with scale etched on the stem, the graduation to be clear-cut and distinct, but quite fine.

(b) *Determination.* Saponify 75 grams of fat in a metal dish with 60 cc. of 30% sodium hydroxide (36° Baumé) and 75 cc. of 95% (by volume) alcohol or 120 cc. of water. Boil to dryness, with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used, boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30% sulphuric acid (25° Baumé) to free the fatty acids, and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using the hot-water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15 or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 by 4 in.) and made of glass about 1 mm. in thickness. Place in a 16-oz. salt-mouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8 by 6 in.), fitted with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermometer, graduated to 0.1° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for thirty seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

<sup>1</sup> U. S. Dept of Agriculture, Bureau of Chemistry Bulletin No. 107, p. 135, 1907.

Place 3 cc. in a test-tube and add 15 cc. of alcohol (95% by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp.gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

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### EDIBLE FATS

These include butter, lard and hardened oils.

Butter is examined for water, fat, ash, curd, and salt; these are usually present in the following proportions:

	Per cent.	Average per cent
Fat.....	78. -90	82
Water.....	5. -20	11
Salt.....	0.4-15	5
Curd.....	0.1- 5	1

These are determined as follows: weigh about 2 grams of butter into a platinum Gooch crucible half filled with ignited fibrous asbestos, and dry it at 100° C. to constant weight. The loss is the amount of *water*. Dissolve out the fat by repeated treatment with petroleum ether and again dry to constant weight. The loss represents the amount of *fat*. Ignite the crucible with a low flame or in a muffle, being careful not to volatilize the salt, until a light-gray ash is obtained. The loss represents *curd* and the residue *ash*. By extraction of the ash with water, and neutralization with calcium carbonate, the salt can be titrated with silver nitrate.

**Examination of the Fat.** Butter is adulterated with oleomargarine, renovated butter, and coconut oil. The first may be detected by testing for cottonseed or sesame oil either by the color tests or by the index of refraction; this at 25° is for butter 1.459-1.462, for oleo. 1.465-1.470. Owing to the fact that butter contains a large per cent of volatile fatty acids (butyric, caproic, caprylic and capric acids, in all about 8%), adulterants may be detected by determining the amount of these. The process usually employed is that of Reichert modified by Meissl.

Five grams of the clear fat, filtered through absorbent cotton, are weighed into a 250-cc. round-bottomed flask and saponified by 2 cc. potassium hydroxide 1 : 1 and 10 cc. of 95% alcohol, under a return flow condenser for twenty-five minutes. The alcohol is rapidly evaporated off on the water bath until no odor of alcohol is perceptible. Add slowly 160 cc. of recently boiled distilled water which has been cooled to 50° or 60°; warm the flask until a clear solution of the soap is obtained. Cool to about 60° and add 8 cc. sulphuric acid 1 : 4 to liberate the fatty acids. Drop into the flask two bits of pumice (about the size of peas) which have been

heated and quenched in water, and tie in a well-fitting cork; warm the flask until the fatty acids have melted and are floating on the liquid. Cool to about 60° and attach the flask to a condenser, using a trap to prevent the sulphuric acid from being mechanically carried over; 110 cc. are distilled into a graduated flask in as nearly thirty minutes as possible. Thoroughly mix the distillate, pour through a dry filter, and titrate 100 cc. with N/10 NaOH, using phenolphthalein as an indicator. Multiply the cc. of alkali by 1.1 and calculate them to 5 grams of fat. The Reichert-Meissl value for butter is from 24 to 34, the average is about 28.8; coconut oil gives 6-8 and other fats less than 1.

The procedure is a conventional one and should be followed as exactly as possible. Coconut and other vegetable oils would be shown by the fact that the unsaponifiable matter would contain phytosterol; also by the Polenske number.<sup>1</sup> Renovated butter is best shown by the "Spoon or Foam Test." This consists in melting a third of a teaspoonful of the sample in a tablespoon over a small flame and stirring with a match. Increase the heat until the fat boils briskly, stirring thoroughly several times. Oleomargarine and renovated butter boil noisily, sputtering like a mixture of grease and water and produce no foam. Butter boils with less noise and much foam sometimes rising over the sides of the spoon. The pieces of curd in butter are much smaller than in either of the others.

**Preservatives.** benzoic, boric and salicylic acids, may be examined according to the procedure given in Woodman and Norton, "Air, Water and Food," pp. 154 and 196.

**Color** may be detected according to Allen, "Commercial Organic Analysis," 4th Ed., Vol. II, or Leach's "Food Analysis."

Lard is adulterated with water, 25% being added in some cases, with cottonseed oil or stearine and beef stearine.

**Water** is determined as with butter; **cottonseed oil** or stearine by the usual tests. It should be borne in mind, however, that hogs fed on cottonseed meal yield a lard which will give the Halphen test as strongly as if it contained 25% of the oil. The iodine number and the presence of phytosterol will confirm this test; the iodine number varies widely according to the source of the fat, but in general it may be said it should be between 46 and 66.

Beef stearine is very difficult if not impossible of detection. For this, reference may be had to Lewkowitsch, 5th Ed., Vol. II.

## HARDENED OILS

As the name denotes, these are oils which have been changed to more or less solid fats by the addition of hydrogen, in the presence of a catalyst, usually a compound of nickel. This betrays their presence and may be tested for as follows:<sup>2</sup>

Ten grams of the fat are heated on the water bath with 10 cc. of hydrochloric acid (sp. gr. 1.12) with frequent shaking for two or three hours. The fat is removed by filtering through a wet filter, receiving the filtrate in a porcelain dish; after partial evaporation of the filtrate 2 or 3 cc. of strong nitric acid are added and the evaporation continued to dryness to ensure the destruction of the organic matter. The residue is dissolved in a few cc. of distilled water, a few drops of a

<sup>1</sup> Z. Nahr. Genussm., 7, 193, 1904, also Leach "Food Analysis."

<sup>2</sup> Kerr, J. Ind. and Eng. Chem., 6, 207, 1914.

1% solution of dimethyl glyoxime in alcohol added, and a few drops of dilute ammonia. The presence of nickel is shown by the appearance of the red-colored nickel dimethyl glyoxime. The amount of nickel can be determined colorimetrically by comparison with solutions containing known quantities.

The quantity of nickel is very minute, not as much as the fats take up when cooked in nickel or nickeled dishes and need cause no apprehension.

Hydrogenation destroys all the characteristics, particularly the color tests, by which the different oils may be sometimes detected.

## WAXES

These, as will be remembered, contain no glycerine; the tests applied to them are the same as to the oils. The characteristics of the more commonly occurring waxes are given in the table, p. 1150; sperm oil, which is really a liquid wax, is included among the oils.

## MISCELLANEOUS OILS AND LUBRICANTS

PROPERTIES OF SOME OF THE MINERAL OILS

Oil	Specific gravity, deg. Baumé at 60° F.	Flash point, °F.	Viscosity (Saybolt), at 70° F.	Cold test, deg. Fahr.
Black.....	29	325	100-120	5-15
Ice machine.....	26-27	325-350	60-100	0-4
Crank case.....	26-27	455	100	
Transformer.....		340-380	400	25
Turbine.....	30	420	160	
Spindle.....	30-35	325-350	58-156	
Loom.....	28	300	203	
Engine.....	27-30	410	190-210	
Cylinder.....	23-25	525	200-300*	
Cylinder.....	26-28	400-575		

\* At 312° F.

Belt Dressings are (1) mixtures of fats, waxes, degreas or tallow with castor or fatty oils; (2) vulcanized corn or cottonseed oil thinned with naphtha; (3) preparations containing wood tar; or (4) preparations containing rosin, which is undesirable. Black oils, car oils, well oil or reduced oils are crude oils from which the naphthas and burning oils have been separated by distillation. Crank-case oils are pure mineral oils which emulsify but little with water. Milling-machine or soluble oils are lard, sulphonated oils or mineral oils held in suspension in water by soaps or alkalies, as borax or soda; the soaps used are either ammonium, sodium or potassium with resin, oleic or sulphofatty acids. Rosin oils are obtained by distilling or "running" rosin, each distillate being called a "run" and numbered according to the times it has been distilled. They oxidize quite rapidly and should not be used as lubricants except as soaps in lubricating greases. Screw-cutting oils are often mixtures of 27° B<sub>é</sub>. paraffin and 25% fatty oil, preferably cottonseed, although lard oil was formerly used. Stainless oils are spindle or loom oils mixed with fatty oils—lard or neatsfoot. Transformer oils should be either pure mineral or rosin oils and as free as possible from water.



acid, alkali and sulphur. Turbine oils should be of excellent quality, free from acid and tendency to resinify, and low in sulphur. Watch oil is obtained from the porpoise, dolphin, or blackfish, where it exists in cavities in the jaw and in the brain or "melon" of the fish. Lubricating greases are mixtures of soaps of palm oil, tallow or rosin oil (with lime or soda as bases) with various oils or fats such as rosin, tallow or mineral oil. The best are those made from tallow by saponification with caustic soda. They may also contain finely powdered talc or graphite. Non-fluid oils are oils or their greases stiffened with "oil pulp" or "dope," i.e., aluminum oleate or palmitate.

The source, preparation and uses of the various oils and greases are described in Rogers and Aubert's *Industrial Chemistry*, Chapters XXII, XXIV, XXV and XXVII.

For the guidance of the analyst, the characteristics of the more frequently occurring oils are given, the usual figures being given in *italic*.

The vegetable oils may be classified into

**Drying.** Linseed, Chinese wood, poppyseed, sunflower and menhaden.

**Semi-drying.** Corn, cottonseed, sesamé, rape, black mustard and horse.

**Non-drying.** Castor, almond, peanut, olive, cocoanut, palm, seal, cod-liver, elaine, lard, neatsfoot, tallow, sperm and whale.

#### References

- Lewkowitsch, "Technology and Analysis of Oils, Fats and Waxes." 3 vols., 5th edition  
Gill, "A Short Handbook of Oil Analysis," 9th edition.  
Battle, "Industrial Oil Engineering."  
Lockhart, "American Lubricants."

## CHARACTERISTICS OF THE FATTY ACIDS FROM SOME OILS

Oil.	Refr. Ind. at -60° C.	M.pt. °C.	Solidifn. Pt. °C.	Iodine Per cent.
Almond .....	1.4461	13-14	9-11.8	93.5-96.5
Castor .....	1.4546	11	3	86-88
Chinese wood .....	—	40-43.8	31.2	145-159.4
Cocanut .....	1.4295	24-27	15-20	8.4-9
Codliver, Medicinal. ....	—	—	17-18 (titer)	164-171
Corn .....	—	18-21.6	14-16	113-125
Cottonseed .....	1.446	34-40	32-35	105-112
Elaine .....				
Horse .....		37.5-39.5	33.6-37.7	84-87
Lard .....		35		
Linseed .....	1.4546	17-24	13-17	179-209.8
Menhaden .....	No figures available.			
Black Mustard .....	1.4665 at 20°	9-17	6-8	108-126.5
Neatsfoot .....	—	28.5-29.8	16-26.5 (titer)	62-77
Olive .....	1.4410	19-31	17-24.6	86-90
Palm .....	—	47.7-50	36-46 44	53.3
Peanut .....	1.4461	27-35	22-32.5	95-103
Poppyseed .....	1.4506	20-21	16.5	139
Rape .....	1.4491	16-22	16-18	99-105
Seal .....	—	14-33	13-17	186-202
Sperm .....	1.4461	23-32	18-26	109-112
Sperm .....	—	13-21	16	85-104
Sunflower .....	1.4531	17-24	17-18	124
Tallow .....				
Whale .....	—	14-27	23-24	130-132

## CHARACTERISTICS OF SOME OILS

Oil	Sp. Gr. 15° C.	Refr. Ind. 15° C.	Volenta °C.	Elaidin.	Mau- ment °C.	Sap. No. mg.	Iodine %	Composition.	Common Adulterants.	Visc. U. Rec. 100° F.	Flash pt., °F.
Almond	0.914- .920 .918		110	Fluid	53	190-195.4	93-101 97	Olein, linolein.	Peach and apricot kernel, cottonseed, peanut, lard, olive, sesame and poppyseed.		
Castor	0.959- .968	1.4795- 4803	Soluble	Solid	46-47	176-186	81-90	Ricinolein, stearin, dihydroxy stearin.	Blown oils, linseed, rape, cottonseed and resin.	1485	505
Chinese wood ortung oil	0.940- .944	1.503 at 19°	40-47	Liquid and solid	—	190-197	156-176	Olein, elacomargarin.			
Cocoanut	0.926 0.874 at 90° C.	1.4573	—	—	—	225-268	8-10	Caproin, caprylin, caprin, olein, laurin, myristicin, palmitin, stearin.	Rarely adulterated.		
Codliver, medicinal	0.922- .941	1.478- 1.481	—	Liquid and solid	100-116	183-188	135-193	Palmitin, stearin, jec- olein, therapin	Salmon, seal, whale, shark liver; oils from other Gadidae are not, commer- cially speaking adulter- ants.	187	480
Corn or maize	0.921- .927 .928	1.4768	80	Pasty	56-88 86	189-193 191	111-123 115	Palmitin, arachidin, olein, linolein.	Rarely adulterated.		
Cottonseed	0.921- .930 .928	1.4737- 4757	90-110	Pasty	70-90 76	191-198	101-117 108	Stearin, palmitin, olein, linolin, arachi- din.	Rarely adulterated.		
Elaine or Red	0.899- .908	1.4631 at 25° C.	—	Solid	—	200	90	Olein, palmitin and stearic acids.	Cottonseed and mineral.		
Horse	0.916- .922	1.4652- 4704	54-80	—	40-56	195-197	76-86	Similar to lard but drier.	Rarely adulterated.		
Lard	0.914-.916	1.4674	54-98	Very solid	39-47 43	190-196	60-88	Olein, stearin, palmi- tin.	Cottonseed, tallow, corn and mineral.	214	505
Linseed	0.9315- .9371 0.938- .946	1.4835	57-79	Liquid and solid portion	103-126 90	187-195.2 189-194	187 8- 205 4 178-190	Isolinolein, linolein, linolin, olein, stear- in, palmitin.	Corn, cottonseed, fish and min.		
Malva	See Corn										

\* With covered glass

Monobases	0.927- 0.930	1.4725	96	As finned	123-128 120	129-193 120	129-193 124	Linolein, myristein, selein, and acotin. stupanodolin.	Mineral and rosin	
Bl't Mustard	0.917-0.919	1.4672	Insoluble	Pasty	42-43	173-176	98-110	Like rapeseed.	Sesamé.	
Neatsfoot	0.915-0.916	1.4695- .4703	62-75	Solid at times	42-49.5	194-199	66-76	Olein, palmitin and stearin.	Other food oils, fish, poppyseed, rape, cotton- seed and mineral oils.	224 440
Olive	0.915- 0.916	1.4703 .4713	85-111	Very Solid	35-47 41	185-203 190	77-84 88	Olein, palmitin, ara- chidin and linolin.	Cottonseed, peanut, rape, sesamé, poppyseed and lard.	
Palm	0.920- 0.924 at 99° C	1.461 at 60°	—	—	—	191-203	53-57	Palmitin, palmitic acid and stearin.	Water, sand and dirt.	
Peanut or Arachis	0.916- 0.917	1.4731	87-112	Solid	46-75 51	185-197 194	83-105 98	Palmitin, linolin, olein, arachidin and lignocerin.	Cottonseed, rape, sesamé and poppyseed.	
Poppyseed	0.924- 0.925	1.4773	—	Pasty	87	190-197 193	133-143 138	Linolin, linolein and lactinololin, olein, stearin, palmitin.	Sesamé.	
Rape or Colza	0.913- 0.916	1.472- .4757	Insoluble	Pasty	49-64 56	188-178 174	94-106 101	Stearin, olein, erucin, rapin, and arachidin	Cottonseed, poppyseed, hempeed, linseed, fish oil	455 247
Seal	0.924- 0.933	1.477	—	Pasty	—	178-196 188	127-193 147	Palmitin, olein, hy- pogaein.	Mineral and rosin.	515 104
Sesamé	0.922- 0.924	1.4748- 4762	87-107	Pasty	63-72	187-194	103-115	Stearin, palmitin, olein and linolin	Cottonseed, peanut, rape and poppyseed	
Sperm	0.844 880	1.4664- 4673	Insoluble	Solid at times	45-61	123 147	70-98	Contains no glycer- in, palmitic acid.	Whale, mineral, rape, liver and arctic sperm.	455 115
Sunflower	0.924- 0.926	1.4762	—	Pasty	72-76	188-194	119-133	Linolin, olein.		
Tallow	0.916	1.4660 at 25° C	71-76	Solid	85	197	56	Similar to lard.		
Turpentine	See page 617									
Whale	917-0.927	1.4691 at 25°	—	Pasty	88	188-193	110-136	Palmitin.	Seal oil.	515 184

## CHARACTERISTICS OF SOME WAXES

Wax.	Sp.Gr. 15°C	Ref. Index at 40°	M.pt.	Solid Pt.	Sapon. Value.	Acid Value.	Iodine Value.	Composition.	Common Adulterants.
Carnauba	0.99- 999	65-69°	83-91	80-87	79-88	0.3-7.0	5-13.2.	Ceryl and myricyl cerotate, carnaubate and a hydrocarbon.	Stearic acid, ceresin and paraffin.
Candelilla	0.969 .993	At 71.5° 1.455	65-68	63-68	46-65	10-21	14-36.8	Hydrocarbon, myricyl alcohol	Like carnauba wax.
Beeswax	0.959- .970	At 75° 1.439- 1.445	62-70	60-63	87-107	16.8-21	7.9-11	Cerotic and melissic acids, myricin, ceryl and myricyl, alcohols, hydrocarbons.	Water, mineral matter, flour, starch, tallow, stearic acid, other waxes, rosin.
Chinese or Insect	0.970	—	80-81	80-83	80-93	51% fatty acids	1.4	Ceryl cerotate.	
Spermaceti	0.905- .960	—	41-46	41-47	120- 134.6	49-53% fatty acids	3.8	Cetyl palmitate.	Stearic acid, beeswax, tallow, paraffin.
Woolfat or wax	0.941- .97	—	Acids 31-42	Acids 40	82-130	—	15-29	Ceryl and carnaubyl alcohols, cholesterol, lanoceric, lanopalmitic, myristic, and carnaubic acids.	
These two below are really fats but are called waxes.									
Japan	0.975	—	50-51	48-50.8	217- 237.5	—	4.2-15.1	Palmitin and palmitic acid.	Water, starch, other fats.
Myrtle	0.995	At 80° 1.436	40-48	39-45	205-217	—	1.9-3.9	Palmitin.	

MULTIPLYING FACTORS TO REDUCE SAYBOLT TIMES TO ENGLER NUMBERS OR TO REDWOOD TIMES<sup>1</sup>

Saybolt Times Seconds.	Factor Saybolt Time to Engler Number.	Factor Say- bolt Time to Redwood Time.	Saybolt Times Seconds.	Factor Saybolt Time to Engler Number.	Factor Say- bolt Time to Redwood Time.
28	0.0357	0.95	76	0.0289	0.86
30	.0352	.95	80	.0285	.85
32	.0346	.94	85	.0284	.86
34	.0342	.94	90	.0282	.85
36	.0337	.94	95	.0280	.85
38	.0334	.93	100	.0279	.85
40	.0330	.93	110	.0276	.85
42	.0327	.92	120	.0274	.84
44	.0323	.92	130	.0272	.84
46	.0320	.91	140	.0271	.84
48	.0317	.91	150	.0269	.84
50	.0314	.90	160	.0268	.84
55	.0306	.90	180	.0267	.84
60	.0300	.89			
65	.0297	.88	1800	0.0267	0.84
70	0.0293	0.87			

The Engler number is the quotient of Engler Time divided by the water value of the instrument at 20° C. in seconds.

## Reagents

The reagents used in oil analysis are few and easily obtained. A list and their method of preparation is here given.

**Acetic Acid, Glacial.** Baker and Adamson's C. P., 99.5% pure. The determination of its strength should be made by titration and not by specific gravity, as the 98% and 80% acid have the same specific gravity, 1.067. The determination of the melting-point gives results equally good with those obtained by titration and requires less time.<sup>2</sup> It is made after the manner of the "titer test" (p. 598), the tube being half filled, chilled to 10 to 11° C., and further chilled by placing the outside bottle in ice-water; the temperature of the super-cooled acid rises to its melting-point, where it remains stationary for some time. The melting-points of acids of various strengths are as follows: 100%, 16.75° C.; 99.5%, 15.65°; 99%, 14.8°.

For Hanus's solution it must not reduce potassium bichromate and sulphuric acid.

**Acetic Anhydride.** Baker and Adamson's C. P.

**Alcohol.** Commercial "Cologne Spirits." For the preparation of alcohol free from aldehyde for alcoholic potash, cologne spirits are treated with silver oxide as follows: 1½ grams of silver nitrate are dissolved in 3 cc. of water, added to 1 liter of alcohol and thoroughly shaken; 3 grams of potassium hydrate are dissolved in 15 cc. warm alcohol and, after cooling, added to the alcoholic silver nitrate and thoroughly shaken again, best in a tall bottle or cylinder. The silver oxide is allowed to settle, the clear liquid siphoned off and distilled, a few bits of pumice, prepared by igniting it and immediately quenching under water, being added to prevent bumping. Alcohol for use in the free acid determination is prepared by placing 10 to 15 grams of dry sodium carbonate in the reagent bottle, taking care to filter it before use.

**Alcohol, Amyl.** Baker and Adamson's C. P.

**Bromine.** The commercial article; also a N/3 solution, made by dissolving 26.6 grams bromine in 1 liter carbon tetrachloride.

<sup>1</sup> Proc. Am. Soc. Test. Mat., 15, 1, 288, 1915.

<sup>2</sup> McIlhenny et al., J. Am. Chem. Soc., 29, 1224, 1907.

*Calcium Chloride.* The dry and also the crystallized salt.

*Calcium Sulphate.* Plaster of Paris.

*Carbon Tetrachloride.* Baker and Adamson's C. P. or Kahlbaum's "Tetrachlor-kohlenstoff."

*Chloroform.* Squibb's, U. S. P.

*Copper.* Copper turnings or clippings, used for the generation of nitric oxide.

*Copper Wire.* Cut in pieces of 0.3 to 0.5 gram.

*Ether.* Squibb's, U. S. P.

*Gasoline.* Gasoline, 86° Baumé.

*Hydrochloric Acid,* C. P.—Specific gravity 1.2. For N/2 HCl dilute 39 cc. of the above acid to 1 liter and standardize.

*Iodine Solution.* Fifty grams of iodine to 1 liter of alcohol. For Hanus's solution dissolve by warming 13.2 grams iodine in 1 liter glacial acetic acid; cool and add 3 cc. of bromine.

*Lead Acetate.* One hundred grams of the salt to 1 liter.

*Lacmoid.* Three grams per liter of dilute alcohol.

*Lacmoid Paper.* Unsized paper dipped in above solution.

*Litmus Paper.*

*Mercuric Chloride.* Sixty grams of the salt to 1 liter of alcohol.

*Nitric Acid.* Specific gravity 1.34.

*Phenolphthalein.* One gram of the substance to 500 cc. of alcohol.

*Meta-Phosphoric Acid.* A saturated solution of the commercial "stick phosphoric acid" in absolute alcohol.

*Potassium Bichromate.* Dissolve 3.8633 grams of the C. P. salt in 1 liter of water; 1 cc. is equivalent to 0.01 gram of iodine. The solution should be tested against iron wire containing a known percentage of iron.

*Potassium Hydrate.* N/2: Dissolve 30 grams of "potash by alcohol" in 1 liter of alcohol. N/6: Dissolve 10 grams of "potash by alcohol" in 1 liter of water and dilute to proper strength. The solution should be protected by "stick potash" from the carbon dioxide in the air. Ten per cent.: Dissolve 100 grams of "stick potash" in 1100 cc. of alcohol.

*Potassium Iodate.* A 2% solution.

*Potassium Iodide.* One hundred grams of the commercial salt are dissolved in 1 liter of water. This should be free from iodate, shown by yielding no coloration when acidified with strong HCl.

*Silver Nitrate.* Thirty grams to 1 liter+0.4 cc. HNO<sub>3</sub>.

*Sodium.*

*Sodium Chloride.* Ordinary "coarse fine" salt for freezing mixtures.

*Sodium Hydrate.* 36° Baumé. Dissolve 300 grams of caustic soda in 1 liter of water.

*Sodium Nitroprusside.* The commercial salt.

*Sodium Thiosulphate.* N/10: Dissolve 26 grams of "sodium hyposulphite" in 1 liter of water.

*Starch Solution.* Rub up in a mortar 1 gram of potato starch, with 10 to 15 cc. of water, pour this into 200 cc. of water which is boiling actively, and continue the boiling for a few minutes.

*Sugar.* Ordinarily granulated sugar.

*Sulphur.* A 1.5% solution in carbon bisulphide.

*Sulphuric Acid,* C. P. This should be at least 99.5% pure, and its strength be determined by titration, as 100% and 94.3% acid have the same specific gravity.

*Dilute.* One part acid to ten parts water.

*Nitrosulphuric Acid,* for the Elaidin Test. A liter of sulphuric acid of 46° Baumé (1.47 specific gravity) is prepared by diluting 560 cc. commercial sulphuric acid to 1 liter; a few drops of nitric acid are added and nitric oxide (generated from copper and nitric acid) passed in until it is saturated. The acid is then cooled in ice-water and the gas passed in until it is saturated at 0° C. This is called Roth's liquid.

The author wishes to acknowledge his indebtedness to Mr. Thomas T. Gray for his careful review of this chapter. Mr. Gray's broad experience in petroleum products as Chief Chemist of Tidewater Oil Company, makes his criticism and suggestions of special value.

<sup>1</sup> Richmond, J. Soc. Chem. Ind., 9, 479, 1890.

# ANALYSIS OF COMMERCIAL SOAPS AND SOAP PRODUCTS

ARCHIBALD CAMPBELL<sup>1</sup>

The following methods of analysis for Commercial Soaps and Soap Products are the Standard Methods adopted by the Committee on Analysis and Specifications of Commercial Soap and Soap Products of the American Chemical Society.

The methods are intended to cover commercial soaps, washing powders, cleansers and liquid soaps, but the methods were not intended to cover highly specialized soaps or toilet preparations, which are designed for some particular use and would require special methods of analysis depending on these special features.

In the case of Unsaponifiable Matter, two methods are given as it was felt that in the case of soaps that contained considerable quantities of Lanolin, Tung Oil, or low-grade Rosins, the gasoline extraction method might show low results. In regular practice, however, the gasoline method is generally preferred.

In the Determination of Rosin, two methods are given. The Twitchell and Wolff Methods. Both appear to be equally accurate but the Wolff method is much quicker and easier to manipulate, hence should be given preference where time is an important factor.

In the Determination of Total Fatty Acids, the final drying should be done in an atmosphere of some inert gas where the soap contains appreciable quantities of drying fats or oils.

## STANDARD METHODS FOR THE SAMPLING AND ANALYSIS OF COMMERCIAL SOAPS AND SOAP PRODUCTS

### Sampling

Take samples from at least 3 per cent of the containers, taking one bar, or package, or in bulk goods, at least one-half pound, or one-half pint in case of liquid soap, from each container. In quantities of less than 100 containers, take at least three samples. Wrap bar samples tightly in paraffined paper at once, and seal by rubbing edges with a heated iron. If possible, place the wrapped bar in an airtight container, in which it should fit very closely. Chip soap and powders are to be sealed air tight in completely filled containers. Liquid soap is to be placed in clean, dry bottles or cans which should be completely filled and securely stoppered with new corks. All samples should be kept cool until tested. In drawing sample of bar, cake, or package goods, the gross weight of final sample to be sent to any one laboratory shall be recorded at the time of taking and sealing.

<sup>1</sup>Chairman of Committee on methods of Analysis and Specifications on Commercial Soap and Soap Products of the American Chemical Society. Vice President, The Globe Soap Company.



### Preparation of Sample

**Bar Soap.** Run complete separate analyses on 25 per cent of the individual bars taken and in no case run less than two analyses. The average of these analyses is to be taken as that of the lot. For these analyses, quarter the bar by cutting at right angles in the center and shave equally from all freshly cut surfaces sufficient soap for the analyses. In case of soaps that can be easily powdered, the entire sample may be run through a suitable food chopper.

**Liquid Soap.** No preparation of the sample, other than thorough mixing, is necessary unless it is received during very cold weather, when it should be allowed to stand at least 1 hour after it has warmed up to room temperature (20° to 30° C.) before it is noted whether it forms a satisfactory lather.

**Powdered and Chip Soaps.** Rapidly disintegrate and mix the sample and weigh out all the portions for the analyses.

Unused portions of the original sample shall be preserved in sealed airtight containers in a cool place.

### Analysis

**Combined Alkali, Neutral Soap, Fatty Anhydride.** Dissolve 10 g. of soap in about 100 cc. of water in a weighed 400 cc. Erlenmeyer flask. When solution is complete, add dilute sulfuric acid in slight excess, insert a small funnel in the neck of the flask, and heat the flask on a steam bath until the fatty acids float on top in a clear, oily layer. Avoid a higher temperature than 80° C. Allow to cool. For the extraction of the fatty acids, redistilled gasoline of boiling point below 65° C. should be used. Pour the contents of the flask, both fatty acids and acid water, into a 300 cc. Squibb's separatory funnel, washing out any adhering fat from the flask with gasoline, and make the first separation, saving the acid water for further extractions, using 50 to 75 cc. gasoline. Wash the gasoline solution in the separatory funnel two or three times with small amounts of distilled water (15 to 25 cc.) avoiding too violent agitation to prevent emulsifying. The last washing should be free from sulfates. Draw off the wash water and emulsion down to the gasoline layer into the acid liquor. Filter the gasoline solution through a filter wet with gasoline into a 500 cc. beaker flask, care being taken to introduce no water into the filtering funnel. The filter should be three-fourth to 1 inch below the rim of the funnel when in place. Now extract the acid water using 50 cc. gasoline for the first extraction. Wash as before and filter the gasoline into the flask. For the two succeeding extractions of the acid water smaller quantities of gasoline suffice, but at least 25 cc. should be used. Wash the filter free from fatty acids. This is best done by allowing to drain well, then tucking in the upper edges of the filter and washing with a spray from a wash bottle. Save the acid water for chloride determination.

Add 100 cc. freshly boiled neutral 95 per cent alcohol to the solution in the flask and titrate with standard sodium hydroxide to exact neutrality, using phenolphthalein as indicator. Transfer without filtering to a tared 150 to 200 cc. Soxhlet flask on the steam bath. Evaporate the gasoline and the alcohol as much as possible. A small stirring rod should be tared with the Soxhlet flask to be used for breaking up the soap to insure complete drying. Dry to constant weight in the oven at not over 105° C. Weigh as soda soap.

This fatty matter naturally includes any mineral oil, neutral fat, and rosin acids, which, if determined separately, must be deducted from the result to obtain the true fatty soap. Calculate the combined sodium oxide ( $\text{Na}_2\text{O}$ ) and deduct from weight of soda soap, giving the fatty anhydride. If original soap was potash soap, proper calculation must be made to reduce to potassium oxide ( $\text{K}_2\text{O}$ ). In case the soap shows an excess of free fatty acid, proper corrections must be made in calculating the combined alkali in the original soap.

**NOTE.** A blank test should be made on the sodium hydroxide solution for neutral salts and the proper corrections made if necessary.

**CHAIRMAN'S NOTE.** In view of some recent coöperative work by the Total Fatty Acid Committee of the Society of Cotton Products Analysts, it will be well to check the drying of the soap in a vacuum oven or in an atmosphere of inert gas, especially where a drying oil is present in quantity in the soap.

### **Free Caustic or Acid, Free Carbonate, Silicate, Water, Insoluble Matter, Borax, Phosphate, Starch, Etc.**

Digest hot a 10-g. sample of soap with 200 cc. high proof (94 per cent or higher) ethyl alcohol, freshly boiled and neutral to phenolphthalein, in 250 cc. beaker. Filter with suction through a neutralized counterpoised filter paper and protect the solution during the operation from carbon dioxide and other acid fumes. Wash the residue on the filter with hot neutral ethyl alcohol until free from soap. Titrate filtrate, using phenolphthalein as an indicator, and calculate the alkalinity to sodium hydroxide or potassium hydroxide, and acidity to oleic acid. Dry the filter papers and weigh as alcohol-insoluble.

**NOTE.** If starch is present, remove water-soluble in warm water without heating above 60° C. Determine starch<sup>1</sup> as follows:

Stir a convenient quantity of the sample (representing from 2.5 to 3 g. of the dry material) in a beaker with 50 cc. of water for an hour. Transfer to a filter and wash with 250 cc. of water. Heat the insoluble residue for two and one-half hours with 200 cc. of water and 20 cc. of hydrochloric acid (sp.gr. 1.125) in a flask provided with a reflux condenser. Cool, and nearly neutralize with sodium hydroxide. Complete the volume to 250 cc., filter, and determine the dextrose by the gravimetric method for determination of dextrose given under method of determining sugar in soap. The weight of dextrose obtained multiplied by 0.90 gives the weight of starch. If sugar is also present, a correction must be made for the starch found. Refer to method of determining sugar in soap.

<sup>1</sup> Method A, Bureau of Chemistry Bulletin 107, p. 53; given also in the "Handbook of Sugar Analysis," C. A. Browne, 1912 Ed., p. 439.

**Analysis of Alcohol-Insoluble**

**Water-Insoluble.** Take up with hot water, filter, wash with hot water, dry and weigh residue as water-insoluble. (Make qualitative test on residue to determine its nature.)

**Water-Soluble.** Dilute filtrate from water-insoluble to 250 cc. In aliquot parts of this solution determine:

1. Total alkalinity by titration with methyl orange as indicator.
2. Borax by using the solution from 1. Boil under a reflux condenser several minutes to remove carbon dioxide. Wash out the condenser with water. Render the boiled solution exactly neutral to methyl orange. Cool and add 20 cc. glycerin. Titrate with  $N/2$  sodium hydroxide, using phenolphthalein as an indicator, until the end-point is reached. Add 10 cc. more of glycerin and note if the red coloration disappears. If it does not disappear, as is usually the case, sodium hydroxide is added until the red color reappears. Another 10 cc. of glycerin is added, and the process repeated until a sharp color change takes place which does not disappear on the addition of more glycerin. Figure as boric oxide or borax as required.
3. Carbon dioxide by absorption method.
4. Silica ( $\text{SiO}_2$ ) by any suitable method.
5. Phosphates by any suitable method.

**Moisture and Volatile Matter**

Weigh out 10 g. of the sample. Dry to constant weight in oven at a temperature not exceeding  $105^\circ \text{C}$ . Report loss in weight as moisture and volatile matter.

**NOTE.** After drying for an hour, time can be saved by adding 50 cc. absolute alcohol and then continuing the drying process in the oven.

**Chloride**

The acid water from which the fatty acids have been separated is carefully saved and neutralized with chlorine-free alkali. The chloride is titrated with standard silver nitrate solution, using potassium chromate as indicator and the results calculated to sodium chloride or potassium chloride as the character of the soap indicates.

### Unsaponified and Unsaponifiable

**NOTE.** The Committee has been unable to agree upon a single solvent for unsaponifiable and invites comparisons and criticisms of the two methods given.

**Ethyl Ether Method.** Weigh 5 g. of the soap into a beaker and dissolve in about 100 cc. of 50 per cent alcohol on the steam bath. If the sample has been found to contain free fatty acid, add just enough aqueous alkali to neutralize this. Evaporate off the bulk of the alcohol, take up with about 200 cc. of hot water and transfer to a separatory funnel of about 500 cc. capacity, designated as No. 1. When cool, rinse out the beaker with about 50 cc. of ether and add it to the soap solution. Shake thoroughly for one minute. By the addition of small amounts of alcohol (5 cc. portions and the total not to exceed 25 cc.), a clear and rapid separation of the aqueous and ether layers is effected. After adding each alcohol portion, the separatory funnel is not shaken but merely given a whirling movement. The aqueous portion is drawn off into another separatory funnel, designated as No. 2. The ether solution is washed with 10 cc. portions of water until this water is no longer alkaline to phenolphthalein. All these washings are added to funnel No. 2 and this solution is extracted with 20 cc. portions of ether until the ether is absolutely colorless (3 or 4 extractions should be sufficient). These ether extracts are combined in a third separatory funnel (No. 3) and washed with 10 cc. portions of water until the water is no longer alkaline to phenolphthalein. The ether in Funnel No. 3 is now added to that in Funnel No. 1, a small amount of ether being used to rinse out Funnel No. 3. The ether solution is now washed with 20 cc. of 10 per cent hydrochloric acid solution and then successively with 20 cc. portions of water until the water is no longer acid to methyl orange. The ether solution is then filtered through a dry filter paper into a weighed beaker or flask. The ether is evaporated or distilled off on the steam bath and the residue is heated with alcohol and, when cool, it is neutralized with standard alkali, using phenolphthalein. Any appreciable amount of fatty acid found is deducted from the weight of the residue. This residue consists of the unsaponifiable and any neutral fat that may have been present in the soap, in which case, saponification of the residue is necessary and a second residue is obtained which will represent the unsaponifiable matter only. The difference between the weights of the two residues is, of course, the neutral fat.

**Gasoline Method.** Dissolve 5 g. of soap in 20 cc. 70 per cent ethyl alcohol, transfer to a Squibb's separatory funnel, using 20 cc. 30 per cent ethyl alcohol to wash out the first vessel used. Cool to room temperature and extract with 5 portions of 50 cc. gasoline (boiling point below 65° C.), in same manner as under fatty anhydride. Wash the gasoline extracts with three portions of 25 cc. each of 10 per cent alcohol. Transfer the gasoline solution to a weighed beaker, evaporate on the steam bath under a current of air, dry in oven at 105° C. to constant weight.

**NOTE.** Test unsaponifiable for soap.

### Rosin<sup>1</sup>

**NOTE.** The Wolff method is much more convenient and rapid than the Twitchell. The committee requests coöperative work to compare the accuracy of these methods before making a choice.

**Twitchell's Method.** Weigh out accurately into a dry filter flask from 3 to 5 g. of the filtered and dried fatty acids prepared from soap. Dissolve this sample in ten times its volume of absolute alcohol, place the flask in ice water and pass a current of dry hydrochloric acid gas through the solution until there is no further absorption of gas. Cork tightly and let stand for two hours, shaking occasionally. During this time, the esters of the fatty acids and the rosin acids will separate as oily drops on the surface of the liquid. Add about 400–500 cc. of water and a small piece of granulated zinc to prevent bumping and boil until the solution is clear. Transfer to a separatory funnel and make repeated extractions with ether as in the determination of fatty acids. The ether extract is washed repeatedly with distilled water until washings are neutral to methyl orange. About an equal volume of freshly boiled alcohol, neutral to phenolphthalein, is then added to the ether extract and the whole is titrated with standard sodium hydroxide solution, phenolphthalein being used as an indicator. Each cubic centimeter of *N* sodium hydroxide solution corresponds to 0.346 g. of rosin in the sample of fatty acid weighed out. Check by evaporation to dryness and weigh as rosin soap. Calculate percentages on original sample.

**Wolff's Method** (*C. A.*, 8 (1914), 2495). Dissolve 3 g. of the dried fatty acids as above in 20 cc. of absolute alcohol. Then add 10 cc. of a solution of one volume of concentrated sulfuric acid (sp.gr. 1.84) and four volumes of absolute alcohol, and boil for 4 min. under a reflux condenser. Add to the liquid about five times its volume of 7 to 10 per cent of sodium chloride solution and extract with ether. Shake out the aqueous portion two or three times with ether. Unite the ether solutions and wash with sodium chloride solution until the washings are neutral. Add 30 cc. neutral alcohol. Titrate the rosin acids with standard sodium hydroxide solution (1 cc. normal alkali = 0.346 g. rosin). Calculate percentage of rosin in original sample.

<sup>1</sup> In a test tube to 5 cc. of the ether extract obtained as stated above, are added 10 cc. of acetic anhydride, the ether is expelled by gently warming (avoid flame) and 1–2 cc. of the residual anhydride is tested for rosin by bringing in contact with it a drop of strong sulphuric acid; a fugative violet color at the junction of the acids indicates rosin. The test may be made on a white porcelain surface.

### Sugar

**Reagents.** (a) *Copper sulfate solution.* 34.639 g. of crystallized copper sulfate are dissolved in water and made up to 500 cc. (b) *Alkaline tartrate solution.* Dissolve 173 g. of Rochelle salts and 125 g. of potassium hydroxide in water and dilute to 500 cc.

Place 10 g. of soap in a 500 cc. Erlenmeyer flask and dissolve in 100 cc. of distilled water. Cool the solution down to 68° C. Add 11 cc. concentrated hydrochloric acid and maintain at this temperature for 15 min. By this treatment the sugar in the soap should have been completely inverted, the soap being decomposed, and the free fatty acids floating on top. Cool until the free fatty acids are completely solidified. Filter and wash into a 250 cc. graduated flask. Before flask is filled neutralize the solution with a strong caustic solution, using methyl orange as indicator. Bring to room temperature and make up to volume. The sugar is determined in an aliquot part of this solution, Allihn's method<sup>1</sup> being used as follows:

Place 30 cc. of the copper sulfate solution, 30 cc. of the alkaline tartrate solution, and 60 cc. of water in a beaker and heat to boiling. Add 25 cc. of the invert sugar solution which must be so prepared as not to contain more than 0.250 g. of dextrose, and boil for 2 min. Filter at once, without diluting, through a Gooch crucible which has been previously prepared and weighed. Wash with hot water and dry to constant weight at 105° C. By referring to Allihn's table for the determination of dextrose,<sup>2</sup> the corresponding amount of dextrose can be obtained. This, multiplied by 0.95 and divided by 10, gives the percentage by weight of the sugar in soap.

**Note.** If starch is present, it must be determined upon alcohol-insoluble, and correction made.

The acid liquor from the fatty acids determination is neutralized with barium carbonate and the whole evaporated over a steam bath to near dryness. The mass of barium sulfate and carbonate containing glycerin is now extracted with a mixture of absolute ethyl alcohol and ether (one part ether to three parts of ethyl alcohol by volume). The alcohol-ether solution is filtered directly into an acetylation flask. The extractions should be made by the use of numerous small portions of the solvent. Care should be taken to see that all lumps are broken, and the whole mass and filter well washed before the acetylation flask becomes filled. (Note: If flask will not hold filtrate, evaporate in a large flask. Boil up the concentrate with water, transfer to acetylation flask, and evaporate down.) The flask is now put on the steam bath with a current of air blowing on the liquid and so evaporated until all the alcohol and ether is driven off. Care must be taken that all alcohol is completely removed, also that the evaporation is not continued unnecessarily long, as glycerin is more or less volatile under these conditions. To this is added 7.5 cc. of acetic anhydride and 3 g. anhydrous sodium acetate and the mixture boiled for 1 hr. under a reflux condenser. After cooling to below the boiling point of water,

<sup>1</sup> Bureau of Chemistry, Bulletin 107, pp. 49-53.

<sup>2</sup> Ibid., p. 50. Also in the "Handbook of Sugar Analysis," C. A. Browne, 1912 Ed., Appendix, p. 30.

50 cc. of water at about 80° C. are added through the condenser and the mass in the flask completely dissolved. The solution is next filtered into a flask of about 1000 cc. capacity, the filter carefully washed with carbon dioxide-free water, and the solution cooled to room temperature.

Phenolphthalein is added and the free acetic acid neutralized with *N* sodium hydroxide solution free from carbonates. Care must be taken that no portion of the solution becomes at any time strongly alkaline or that the end-point is passed, as either will cause the saponification of the tri-acetin formed, causing low results. 5 cc. of *N* sodium hydroxide free from carbonates are added. The solution is boiled for one-fourth hour, cooled quickly, and the excess of alkali titrated with *N* acid. A blank on the reagents is run under identical conditions. From the difference between the two titrations, the alkali required to saponify the tri-acetin is determined.<sup>1</sup> (1 cc. *N* sodium hydroxide = 0.03069 g. glycerol.)

**Precautions.** Tri-acetin is volatile with water vapor. Avoid boiling of solution of tri-acetin. Solutions should be free from carbonates as they introduce serious errors with phenolphthalein. Great care must be taken in approaching the end-point when neutralizing the free acetic acid as it is not possible to titrate back.

Sugars affect the acetin method in proportion to the number of hydroxyl groups present.

**Personnel of Committee:**

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<sup>1</sup> For details see Jour. of Ind. and Eng. Chem., 3 (1911), 682.

# ANALYSIS OF PAINTS

HENRY A. GARDNER<sup>1</sup> AND JOHN A. SCHAEFFER<sup>2</sup>

In reporting the results of an examination of a paint, it is advisable to give all the analytical data as well as a résumé showing the probable composition of the paint. This is shown in the following example:

## RESULTS OF ANALYSIS

Total Pigments or Solids .....	60%
Total Vehicle or Liquids .....	40

### Analysis of Pigment Portion

Lead Oxide (PbO) .....	37.47%
Zinc Oxide (ZnO).....	44.50
Alumina, iron, lime.....	2.90
Magnesia (MgO).....	1.90
Silica (SiO <sub>2</sub> ) .....	4.63
Carbon Dioxide (CO <sub>2</sub> ).....	2.50
Sulphuric Anhydride (SO <sub>3</sub> ) .....	5.02
Water (combined) ..	.73
	<hr/>
	99.15%

### Analysis of Vehicle Portion

Vehicle contained 20% volatile matter.

Volatile matter consisted of equal parts of turpentine and mineral spirits.

Non-volatile matter had:

Iodine Number.....	175
Acid Number.....	2.4
Saponification Number.....	188

and contained .02% ash consisting of lead and manganese oxides.

### Probable Composition of Paint.

Pigment.....	60%
Liquid.....	40

#### Pigment

Basic Carbonate—White Lead.....	22%
Basic Sulphate—White Lead.....	25
Zinc Oxide.....	43
Asbestine.....	10
	<hr/>
	100%

#### Liquid

Raw Linseed Oil.....	80%
Mineral Spirits.....	10
Turpentine and Drier .....	10
	<hr/>
	100%

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## ANALYSIS OF PAINT VEHICLES

**Composition of Liquid Part.** The vehicle or liquid portion of paints may contain various fixed animal, vegetable or mineral oils, oleo-resinous varnishes, turpentine, mineral distillates, benzol and driers.

It is always advisable to determine the total percentage of liquids in a paint. The container should be thoroughly shaken so that the contents will be uniform throughout. A portion of 4 or 5 ounces may then be removed and placed in a screw-cap bottle. The original can of paint should then be set aside so that settling of the pigments will take place. Unless the paint is in paste form, this will usually be accomplished in twenty-four hours. A portion of the clear liquid floating over the pigments may then be removed and directly examined as outlined under Separation of Vehicle Components.

**Percentage of Liquid by Ignition Method.** The percentage of vehicle in the uniform sample of paint previously obtained may be found by placing a weighed portion in a porcelain crucible and slowly igniting it to burn off the organic constituents. By carefully regulating the heat, the oil and volatile thinners will be slowly burned off, leaving the pigment behind, which may then be weighed, calculating the vehicle by difference. This method is a rapid one and works well with some pigments. When pigments are present which show an appreciable loss on ignition, or blacks or blues, this method is not to be relied upon.

**Percentage of Liquid by Extraction Methods.** Another good method of separating the vehicle from a paint is to place a portion in a large tube, adding a considerable quantity of benzol, petroleum ether, or that portion of gasoline distilling below  $120^{\circ}$  C., subsequently centrifuging. Pigments which settle slowly are thrown down very rapidly by this method. The process is repeated three or four times in order thoroughly to free the pigment from oil. After drying, the pigment is weighed and the percentage of vehicle determined by difference. In case a centrifuge is not available, the vehicle of many paints may be separated by simply shaking a portion of the paint in a long test-tube with benzol, allowing the pigment to settle, repeating the extraction until the oil is thoroughly removed.

Some operators have from time to time used a Soxhlet extractor for the determination of the vehicle of a paint. This method is rather slow and does not always give satisfactory results.

It must be remembered that no method of extraction of the oil from a paint will give absolute results. The last traces of oil cannot be removed from the pigment, which is probably due to the fact that many pigments such as lead and zinc react with the oil, producing small quantities of insoluble soaps which are not completely dissolved by the solvent.

In the extraction of paints, the choice of a solvent is important. When benzol ( $90^{\circ}$ ) is not available, it may be replaced by gasoline that has been redistilled, using the light fraction coming over below  $120^{\circ}$  C. This cannot be used, however, when varnish resins other than rosin are present, as they are insoluble therein.

There are some pigments which by reason of their low specific gravity, colloidal nature or partial solubility can never be completely separated from oil, either by settling, centrifuging or extraction. Of these the most commonly met with are lampblack and other forms of carbon, zinc oxide and Prussian blue. Colloidal pigments such as zinc oxide are very troublesome in this respect. When these pigments, however, are present in a paint in considerable percentage, the

difficulty of their separation may be avoided by adding to the paint three or four times its volume of fuller's earth, diluting the mixture in a large test-tube with gasoline or petroleum ether and either centrifuging or placing in a rack to settle. The fuller's earth carries down the colloidal pigments and the separation is sharp and easy. This method, of course, is simply used to extract the vehicle present. The pigment resulting from the separation cannot be used for analysis on account of admixture with the fuller's earth.

In some cases the pigments in paste colors made of lampblack and Prussian blue cannot be separated from the vehicle portion. The amount of Prussian blue present, however, may be determined by making a Kjeldahl-Gunning determination on a portion of the entire paint, multiplying the nitrogen found by 4.4. For the determination of the lampblack present, a portion of the entire paint may be boiled with an excess of alcoholic potash until all of the oil is saponified. The mixture is then decanted through a filter and washed, first with hot alcohol and then with hot water. This affords a very good separation of the vehicle from the pigment of such paints. By this method, the Prussian blue which may be present is partially destroyed, the iron content remaining admixed with the black pigment on the filter.

**Separation of Vehicle Components.** Whenever possible, it is advisable to determine the constituents of the vehicle upon that sample that has been removed from the top of the settled can of paint. A weighed portion of this vehicle may be placed in a tared flask and attached to a Liebig condenser. Heating to  $180^{\circ}\text{C}$ . or lower will drive off nearly all the volatile constituents. The composition of the distillate may be determined by the methods given under the Examination of Turpentine. A portion of the residue in the flask, which consists of oil, driers, gums, etc., may be transferred to a crucible and ignited. The residue may then be weighed and calculated to ash. The ash should be analyzed for lead, manganese and other driers.

Another portion of the original vehicle may be evaporated in an atmosphere of  $\text{CO}_2$  (prevents oxidation) to remove the volatile constituents. A portion of the oil residue may then be examined for iodine number and other constants. In some instances it would be advisable to make a saponification and extraction of the fatty acids from this residue, determining the iodine number on the fatty acids.

**Water.** For a direct determination of the percentage of water in a paint, the analyst may place a weighed quantity (approximately 100 grams) of the paint in a metal still, mixing it with an equal quantity of sand. Distillation will drive off the water and other volatile constituents which will separate into two layers in the graduate.

**Direct Distillation for Volatiles.** For a direct determination of the volatile constituents in a paint, a sample may be distilled *in vacuo*. This is easily managed wherever a vacuum pump is available and avoids the necessity of overheating the oil. When distilling by this method, a sample of the clear vehicle from a settled paint, in order to obtain the fixed oils for analysis, it should not be heated above  $150^{\circ}\text{C}$ . and neither should the solvent be volatilized in such a way as to allow the oil to be in contact with air, as it will oxidize rapidly while warm and its iodine number be very much lowered. The volatile may also be separated by steam distillation.

**Detection of Resinates.** To determine whether the drier in a paint is of the resinate type or linoleate type, a few drops of the oil vehicle may be mixed on a porcelain plate with one or two drops of acetic anhydride, subsequently adding a

drop of sulphuric acid. Upon the addition of the sulphuric acid, a flash of purple color, turning to dark brown, will be shown where rosin is present. If rosin should be present in the vehicle to a considerable extent, the oil will have a very high acid number. The approximate percentage of rosin present may be determined by shaking a portion of the vehicle with 95% alcohol in a separatory funnel, subsequently separating the alcoholic extract, evaporating and weighing the residue.

**Detection of Various Oils.** Chinese wood oil may be detected in the vehicle by mixing the oil with an equal volume of a saturated solution of iodine in petroleum ether, allowing the mixture to stand in direct sunlight. Under these conditions, a peculiar, insoluble, spongy polymer of one of the fatty acids of Chinese wood oil is shown. Fish oil can usually be detected by its odor and the dark red color during saponification. The presence of soya bean and other vegetable oils is in some cases difficult to detect. The iodine numbers of these oils, however, are all lower than that of linseed oil. It must be remembered, however, that the iodine number of boiled linseed oil is lower than that of raw oil and that the iodine number of oils extracted from many paints is usually lower than shown by the original oil. In the presence of considerable quantities of drier, it is always advisable to extract the fatty acids from oil and make the iodine determination upon them.

The distillate from the paint vehicle may consist of turpentine, mineral distillates, benzol and similar solvents. The presence of benzol is readily detected by adding a few drops of the distillate to a small quantity of a mixture of concentrated nitric and sulphuric acids. Upon heating this mixture, the characteristic odor of nitro-benzol will be recognized if benzol is present. Mineral distillates from petroleum are easily detected by the polymerization method given under the Examination of Turpentine.

## ANALYSIS OF PAINT OILS

Although linseed oil is used to the greatest extent in paints, some other oils occasionally find application in the manufacture of special paints. The following have been used for this purpose: soya bean oil, perilla oil, corn oil, cottonseed oil, sunflower oil, lumbang oil and similar vegetable oils; menhaden oil, whale oil, herring oil, and similar marine animal oils of relatively high iodine number.

There are given below methods for the analysis of linseed oil, in accordance with the latest practice developed by the U. S. Government Interdepartmental Committee on standardization of paint specifications. These methods may be followed in examining any of the other oils mentioned above.

**Iodine Number.** Weigh in a small glass capsule from 0.2 to 0.3 gram of oil, transfer to a 500-cc. bottle having a well-ground stopper, dissolve the oil in 10 cc. of chloroform and add 30 cc. of Hanus solution; let it stand with occasional shaking for one hour, add 10 cc. of a 10 per cent solution of potassium iodide and 150 cc. of water, and titrate with standard sodium thiosulphate, using starch as indicator. Blanks must be run each time. From the difference between the amounts of sodium thiosulphate required by the blanks and the determination, calculate the iodine number (centigrams of iodine to 1 gram of oil). The iodine number of raw linseed oil varies from 175 to 193. Make the Hanus solution by dissolving 13.2 grams of iodine in 1000 cc. of glacial acetic acid which will not reduce chromic acid, and adding 3 cc. of bromine.

### Analysis of Linseed Oil

**Loss on Heating at 105° to 110° C.** Place 10 grams of the oil in an accurately weighed 200 cc. Erlenmeyer flask; weigh. Heat in an oven at a temperature between 105 and 110° C. for 30 minutes; cool and weigh. Calculate the percentage loss. This determination shall be made in a current of dry carbon dioxide gas.

**Foots.** With all materials at a temperature between 20° and 27° C. mix, by shaking in a stoppered flask for exactly one minute, 25 cc. of the well-shaken sample of oil, 25 cc. of acetone and 10 cc. of the acid calcium chloride solution. Transfer the mixture to a burette where settling can take place for 24 hours. The temperature during this period should be between 20° and 27° C.

The volume of the stratum lying between the clear calcium chloride solution and the clear acetone and oil mixture is read in tenths of a cubic centimeter or a fraction thereof. This reading multiplied by four expresses the amount of foots present as percentage by volume of the oil taken.

**Specific Gravity.** Use a pycnometer accurately standardized and having a capacity of at least 25 cc., making the test at 15.5° C., water being unity at 15.5° C.

**Acid Number.** Weigh from 5 to 10 grams of the oil. Transfer to a 350 cc. Erlenmeyer flask. Add 50 cc. of neutral 95 per cent ethyl alcohol. Put a condenser loop inside the neck of the flask. Heat on a steam bath for 30 minutes. Cool and add phenolphthalein indicator. Titrate to a faint permanent pink color with the standard sodium hydroxide solution. Calculate the acid number (milligrams KOH per gram of oil).

**Saponification Number.** Weigh about 2 grams of the oil in a 350 cc. Erlenmeyer flask. Add 25 cc. alcoholic sodium hydroxide solution. Put a condenser loop inside the neck of the flask and heat on the steam bath for one hour. Cool, add phenolphthalein as indicator, and titrate with half normal sulphuric acid. Run two blanks with the alcoholic sodium hydroxide solution. These should check within 0.1 cc. N/2 H<sub>2</sub>SO<sub>4</sub>. From the difference between the number of cubic centimeters of N/2 H<sub>2</sub>SO<sub>4</sub> required for the blank and for the determination, calculate the saponification number (milligrams KOH required for 1 gram of oil).

**Unsaponifiable Matter.** Weigh 8 to 10 grams of the oil. Transfer to a 250 cc. long-neck flask. Add 5 cc. of strong solution of sodium hydroxide (equal weights of NaOH and H<sub>2</sub>O), and 50 cc. 95 per cent ethyl alcohol. Put a condenser loop inside the neck of the flask and boil for two hours. Occasionally agitate the flask to break up the liquid but do not project the liquid onto the sides of the flask. At the end of two hours remove the condenser and allow the liquid to boil down to about 25 cc.

Transfer to a 500 cc. glass-stoppered separatory funnel, rinsing with water. Dilute with water to 250 cc., add 100 cc. redistilled ether. Stopper and shake for one minute. Let stand until the two layers separate sharp and clear. Draw all but one or two drops of the aqueous layer into a second 500 cc. separatory funnel and repeat the process using 60 cc. of ether. After thorough separation draw off the aqueous solution into a 400 cc. beaker, then the ether solution into the first separatory funnel, rinsing down with a little water. Return the aqueous solution to the second separatory funnel and shake out again with 60 cc. of ether in a similar manner, finally drawing the aqueous solution into the beaker and rinsing the ether into the first separatory funnel.

Shake the combined ether solution with the accumulated water rinsings and let the layers separate sharp and clear. Draw off the water and add it to the main aqueous solution. Shake the ether solution with two portions of water (about 25 cc. each). Add these to the main water solution.

Swirl the separatory funnel so as to bring the last drops of water down to the stopcock, and draw off until the ether solution just fills the bore of the stopcock. Wipe out the stem of the separatory funnel with a bit of cotton on a wire. Draw the ether solution (portionwise if necessary) into a 250 cc. flask and distill off. While still hot, drain the flask into a small weighed beaker, rinsing with a little ether. Evaporate this ether, cool and weigh. (*The unsaponifiable oil from adulterated drying oils is volatile and will evaporate on long heating. Therefore heat the beaker on a warm plate, occasionally blowing out with a current of dry air. Discontinue heating as soon as the odor of ether is gone.*)

**Iodine Number.** Place a small quantity of the sample in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 grams (0.10 to 0.20 grams) to a 500 cc. bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 cc. of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc. of chloroform to each of two empty bottles like that used for the sample. Add to each bottle 25 cc. of Hanus solution and let stand with occasional shaking for one-half hour. Add 10 cc. of the 15 per cent potassium iodide solution and 100 cc. of water, and titrate with standard sodium thiosulphate using starch as indicator.

The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titration and the titration on the samples and the iodine value of the thiosulphate solution, calculate the iodine number of the samples tested. (Iodine number is centigrams of iodine to 1 gram of sample.)

**Ash.** Take a porcelain crucible or dish. Add 10 to 25 cc. of oil, carefully weighing the amount added. Place on a stone slab on the floor of a hood. Ignite by playing the flame of a burner on the surface of the oil and allow to burn quietly until most of the oil is burned off; then transfer to a muffle or over a flame and continue heating at a very low temperature (not over a dull red) until all carbonaceous matter is consumed. Cool, weigh, and calculate the percentage of ash. Moisten the ash with a few drops of water and test with litmus paper. Record whether neutral or alkaline. Wash any ash adhering to the test paper back into the crucible. Dissolve the ash in dilute nitric acid to which a little hydrogen peroxide has been added. After solution is complete make up the volume to about 50 cc. with nitric acid and water so that the final volume will contain about 1 volume of concentrated nitric acid and 3 volumes of water. Boil to remove excess of hydrogen peroxide. Determine manganese by the bismuthate method.

Ash another portion of the oil and dissolve the ash as above in nitric acid and hydrogen peroxide. Transfer to a 250 cc. beaker and dilute to about 200 cc. This volume of solution should contain 15 to 20 cc. of concentrated nitric acid. Electrolyze this solution using platinum electrodes (the anode being previously weighed) with a current density of about 0.5 amperes and

2 to 2.5 volts. It is best to pass the current overnight (about 15 hours). On removing the anode, it is carefully washed in clear water, dried in a steam oven, transferred to an oven where it is heated to 180° C., cooled and weighed. The increase in weight of the anode multiplied by 0.86 gives the weight of lead in the sample. Calculate to percentage. If desired, the lead may be determined by the sulphate or any other accurate method in place of the electrolytic method given above.

**Time of Drying on Glass.** Flow the oil over a perfectly clean glass plate and allow to drain in a vertical position in a well-ventilated room at a temperature between 15° and 39° C. After about 2 hours the film is tested at intervals with the finger at points not less than 2½ cm. from the edges. The film will be considered dry when it adheres no longer to the finger and does not rub up appreciably when the finger is rubbed lightly across the surface. With boiled linseed oil this usually occurs in from 5 to 18 hours.

### Reagents for Testing

The following reagents will be required:

*Acetone* that will pass the specification of the United States Pharmacopoeia.

*Acid Calcium Chloride Solution.* Saturate with calcium chloride a mixture of 90 parts water and 10 parts concentrated hydrochloric acid (specific gravity 1.2).

*Standard Sodium Thiosulphate Solution.* Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from carbon dioxide in the proportion so that 24.83 grams crystallized sodium thiosulphate will be present in 1000 cc. of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal strength. Preserve in a stock bottle provided with a guard tube filled with soda lime.

*Starch Solution.* Stir up 2 to 3 grams of potato starch or 5 grams soluble starch with 100 cc. of 1 per cent salicylic acid solution, add 300 to 400 cc. boiling water, and boil the mixture until the starch is practically dissolved. Dilute to 1 liter.

*Standard Iodine Solution.* Dissolve 13 grams of resublimed iodine and 18 grams of pure potassium iodide (free from iodates) in 50 cc. of distilled water, and dilute to 1000 cc. Determine its exact value by titrating with the standard sodium thiosulphate solution.

*Potassium Iodide Solution.* Dissolve 150 grams of potassium iodide free from iodate in distilled water and dilute to 1000 cc.

*Hanus Solution.* Dissolve 13.2 grams of iodine in 1000 cc. of glacial acetic acid (99.5 per cent) that will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc. of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

*Standard Sodium Hydroxide Solution.* Prepare a stock concentrated solution of sodium hydroxide by dissolving sodium hydroxide in water in the proportion of 200 grams NaOH to 200 cc. water. Allow this solution to cool and settle in a stoppered bottle for several days. Decant the clear liquid from the precipitate of sodium carbonate into another clean bottle. Add clear barium

hydroxide solution until no further precipitate forms. Again allow to settle until clear. Draw off about 175 cc. and dilute to 10 liters with freshly boiled distilled water. Preserve in a stock bottle provided with a large guard tube filled with soda lime. Determine the exact strength by titrating against pure benzoic acid ( $C_6H_5COOH$ ) using phenolphthalein as indicator. This solution will be approximately one-fourth normal, but do not attempt to adjust it to any exact value. Determine its exact strength and make proper corrections in using it.

*Alcoholic Sodium Hydroxide Solution.* Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 grams per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used; it will keep colorless longer if the alcohol is previously treated with NaOH (about 80 g. to 1000 cc.), kept at about 50° C. for 15 days, and then distilled.

*Half Normal Sulphuric Acid Solution.* Add about 15 cc. sulphuric acid (1.84 specific gravity) to distilled water, cool and dilute to 1000 cc. Determine the exact strength by titrating against freshly standardized sodium hydroxide or by any other accurate method. Either adjust to exactly half normal strength or leave as originally made, applying appropriate correction.

Standards are given below for raw and boiled linseed oil obtained from South American flax. The same specifications obtain for linseed oils from North American flax except that the minimum iodine number of such oil should be 178 for the raw and 176 for the boiled.

#### Raw Linseed Oil

	Maximum	Minimum
Loss on heating at 105 to 110° C. (per cent) . . . . .	0.2	....
Foots by volume (per cent) . . . . .	2.0	....
Specific gravity 15.5/15.5° C. . . . .	.936	0.932
Acid number . . . . .	6.0	....
Saponification number . . . . .	195.0	189.0
Unsaponifiable matter (per cent) . . . . .	1.5	....
Iodine number (Hanus) . . . . .	....	170.0
Color . . . . .	Not darker than a freshly prepared solution of 1.0 gram potassium bichromate in 100 cc. pure strong (1.84 specific gravity) sulphuric acid.	

#### Boiled Linseed Oil

	Maximum	Minimum
Loss on heating at 105° to 110° C. (per cent) . . . . .	0.2	....
Specific gravity at 15.5/15.5° C. . . . .	.945	0.937
Acid number . . . . .	8.0	....
Saponification number . . . . .	195.0	189.0
Unsaponifiable matter (per cent) . . . . .	1.50	....
Iodine number (Hanus) . . . . .	....	168.0
Ash (per cent) . . . . .	.7	.2
Manganese (per cent) . . . . .	....	.03
Lead (per cent) . . . . .	....	.1
Time of drying on glass (hours) . . . . .	20.0	....



### Examination of Tung Oil (Chinese Wood Oil)

The methods given above for the analysis of linseed oil and similar oils may be used for the examination of tung oil except that the iodine number must be determined by the Hubl method as given below; the Hanus method not being satisfactory for tung oil. The heating test and iodine jelly test used for tung oil are also given below as these are used extensively by the chemist for judging the purity and value of tung oil.

**Iodine Number (Hubl).** Place a small quantity of oil into a small weighing bottle or beaker. Weigh carefully. Transfer by dropping from 0.2 to 0.3 gram to a 500-cc. bottle having a well-ground stopper, or a specially flanged neck, iodine-test Erlenmeyer flask. Re-weigh the weighing bottle or beaker to determine the amount of oil used in the test. Then dissolve the oil in 10 cc. of chloroform and add an amount of Hubl solution containing twice the amount of iodine that will be absorbed by the oil. Stopper the flask, shake well, and place in a dark closet for eighteen hours. Add 10 cc. of a 15% solution of potassium iodide and 100 cc. of distilled water. Titrate with N/10 sodium thiosulphate, using starch as an indicator. Blank tests must be made. From the difference between the amounts of sodium thiosulphate required by the blanks and the determination, calculate the iodine number (centigrams of iodine to 1 gram of oil).

On account of the fact that Hubl solution after preparation is apt to deteriorate in strength, it is considered advisable to have prepared the two component parts of Hubl solution, namely, a solution of mercuric chloride in alcohol and a solution of iodine in alcohol, of the proper strength, as outlined in text-books. The proper amounts of these solutions may be mixed on the day of use.

**Heating Test (Browne's Method).** Test-tubes for containing the oil should be 16 cm. by 15 mm., with a mark near the bottom to indicate 5 cc., and closed, by a cork so perforated that a glass rod 3 mm. in diameter can move freely.

Fill a copper beaker (height 12 cm.; internal diameter, 6 cm.) with cottonseed oil to a height of 7.5 cm. Place a thermometer so as to be 1.5 cm. from the bottom of the bath.

Use a nitrogen-filled, immersed-stem chemical thermometer, engraved stem; total length 4 to 4½ ins.; graduated from 210° to 310° C. in 2° intervals; the length between 210° and 310° C. not less than 2½ ins. If preferred, use emergent-stem thermometer 30 cm. long, with graduations from 100° to 400° C., making correction for emergent stem according to the method outlined in Stem Correction Sheet No. 44 of the U. S. Bureau of Standards.

When the bath temperature is 293° C. (560° F.) and very slowly rising at this point, place the tube containing 5 cc. of the oil to be tested so that its bottom is level with the lowest part of the bulb of the thermometer. Note the time, remove the source of heat for about forty-five seconds and then reapply. Before two minutes have elapsed the temperature of the bath will have fallen to 282° C. (540° F.), at which point it should be kept as steady as possible. When the wood oil has been in the bath about nine minutes, raise the glass rod at intervals of one-half minute, and when the rod is firmly set note the time. As setting or jellying takes place within a few seconds of fluidity, a good end-determination is afforded. Remove the specimen at once, heat the bath again to 293° C., and repeat the experiment with another portion of the sample.



No stirrer is used in the bath. A screen around the bath enables the temperature to be more easily reached. When the cottonseed oil has become tarry and viscid, it should be renewed; otherwise heating may be irregular.

**Iodine Jelly Test.** In a wide-necked 200-cc. Erlenmeyer flask, place 2.5 grams (weight correct to 1 milligram) of the oil. Add 10 cc. of chloroform from a pipette and stopper the flask immediately. Carefully insert a small glass vial into the flask so that the vial stands upright. Into the vial from a pipette run 10 cc. of a solution of iodine in chloroform, containing 0.035 to 0.036 gram of iodine per cc. Place the flask in a bath containing water at 25° to 26° C. and allow it to stand there for a few minutes. Keep the flask stoppered, except when it is necessary to remove stopper to insert the vial and to add the iodine solution. Tilt and rotate the flask so that the vial is upset and the contents of the flask are thoroughly mixed, at the same time starting a stop-watch. Keep the flask in the bath at 25° to 26° C. and at the end of every quarter minute tilt the flask towards a horizontal position. Note the time required for the formation of a jelly that does not flow, but sticks to the bottom of the flask or slides as a mass. Record time in minutes and quarters thereof. Pure Chinese wood oil should require  $2\frac{1}{4}$  to  $3\frac{1}{4}$  minutes for the formation of the jelly. If the temperature of the laboratory is more than 2° or 3° C. above or below 25° C., place the flask containing the iodine solution in the bath and allow it to remain there for several minutes before pipetting out the 10 cc. for the test.

A convenient procedure for preparing the iodine solution is as follows: Treat an excess of iodine with warm chloroform and after shaking for a few minutes cool the contents to about 20° C. and filter through glass wool. Pipette 10 cc. of the solution into a flask containing 10 cc. of 10% potassium-iodide solution, and titrate with 0.1 normal sodium-thiosulphate solution. Calculate the iodine content and dilute with chloroform so as to obtain an iodine content of 0.035 to 0.036 gram per cc. After dilution, titrate again against the thiosulphate to be sure that the solution is of required strength.

All the details of the above method must be followed exactly.

The chloroform used to dissolve the oil and to prepare the iodine solution must conform to the requirements of the U. S. Pharmacopoeia and must have a specific gravity at 25/25° C. of not more than 1.481 and not less than 1.480. The proper density can be obtained by washing with water if the specific gravity is too low, or by adding 95% ethyl alcohol if too high.

**Standards for Chinese Wood Oil, A. S. T. M.**

Raw Chinese wood oil should conform to the following requirements:

	Maximum	Minimum
Specific gravity at 15°.5/15°.5 C.....	0.943	0.939
Acid number.....	6	.....
Saponification number.....	195	190
Unsaponifiable matter, per cent.....	0.75	.....
Refractive index at 25° C. ....	1.520	1.515
Iodine number (Hubl eighteen hours).....	.....	165
Heating test (Browne's method) minutes.....	12	.....
Iodine jelly test, minutes.....	4	.....

## CONSTANTS OF VARIOUS OILS

	Sp. Gr.	Iodine No.	Sapon. No.	Acid No.	Refrac. Index.
Raw Linseed Oil.....	.931	185	188	2.0	1.4867
Soya Bean Oil.....	.924	129	180	2.3	1.4813
Menhaden Oil.....	.932	158	187	3.9	1.4850
Raw Tung Oil.....	.944	166	183	3.8	1.5050
Perilla Oil.....	.94	200	188	2.0	1.4874
Perilla Special.....	.94	192	189	3.2	1.4978
Heavy Bodied Linseed Oil.....	.968	133	189	2.8	1.4966
Lithographic Linseed Oil.....	.97	102	199	2.7	1.4978
Whale Oil.....	.924	148	191	9.2	1.4820
Boiled Linseed Oil..... (Linolate Drier)	.941	172	187	2.7	1.4895
Corn Oil.....	.921	124.8	190.1	4.1	1.4800
Cottonseed Oil.....	.920	111.7	194.3	0.9	1.4781
Rosin Oil.....	.964	68.9	35.5	32.4	.....
Treated Tung Oil <sup>1</sup> .....	.882	56.4	101.3	7.7	1.4764
Lumbang Oil.....	.927	152	189	1.0	1.4789
Sunflower Oil.....	.924	124.6	189.3	7.5	1.4796
Henpecked Oil.....	.927	149.4	191.1	3.9	1.4822
Shark Oil.....	.910	132.8	158.9	5.2	1.4815
Sardine Oil.....	.919	134.6	177.3	10.4	1.4800
Petroleum Mixing Oil.....	.851	28.2	52.9	1.1	1.4773
Boiled Linseed Oil..... (Resinate Drier)	.936	184.2	187.6	7.3	1.4895
Peanut Oil.....	.932	102.2	188.0	2.2	1.4790

Boiled linseed oil from North American seed should conform to the following requirements, A. S. T. M.:

	Maximum.	Minimum.
Specific gravity at $\frac{15^{\circ}.5}{15^{\circ}.5}$ C.....	0.945	0.937
Acid number.....	8	
Saponification number.....	195	189
Unsaponifiable matter, per cent.....	1.5	
Refractive index at 25° C.....	1.484	1.479
Iodine number (Hanus).....		178
Ash, per cent.....	0.7	0.2
Manganese, per cent.....		0.03
Calcium, per cent.....	0.3	
Lead, per cent.....		0.1

Raw linseed oil from North American seed should conform to the following requirements, A. S. T. M.:

	Maximum.	Minimum.
Specific gravity at $\frac{15^{\circ}.5}{15^{\circ}.5}$ C.....	0.936	0.932
or		
Specific gravity at $\frac{25^{\circ}}{25^{\circ}}$ C.....	0.931	0.927
Acid number.....	6.00	
Saponification number.....	195	189
Unsaponifiable matter, per cent.....	1.50	
Refractive index at 25° C.....	1.4805	1.4790
Iodine number (Hanus).....		180

<sup>1</sup> Contained 30% volatile matter, largely high boiling-point petroleum spirits.

### Examination of Turpentine

#### RECOMMENDED METHODS OF THE A. S. T. M.

**Color.** Fill a 200-mm., perfectly flat-bottom colorimetric tube graduated in millimeters to a depth of from 40 to 50 mm. with the turpentine to be examined. Place the tube in a colorimeter and place on or under it a No. 2 yellow Lovibond glass. Over or under a second graduated tube in the colorimeter, place a No. 1 yellow Lovibond glass and run in the same turpentine until the color matches as nearly as possible the color in the first tube. Read the difference in depth of the turpentine in the two tubes. If this difference is 50 mm. or more the turpentine is "Standard" or better.

**Specific Gravity.** Determine specific gravity at any convenient temperature with a plummet, the displacement of which has been accurately determined for that temperature, or by an equally accurate method, using the factor 0.00082 for each degree centigrade that the temperature of determination differs from 15° C.

**Refractive Index.** Determine refractive index at any convenient temperature with an accurate instrument, and calculate the results to 15° C., using the factor 0.00045 for each degree that the temperature of determination differs from 15° C.

**Distillation.** Use an ordinary Engler flask and condenser,<sup>1</sup> and heat the flask by placing it in a glycerine or oil bath of the general type described in Bulletin No. 135, Bureau of Chemistry. Fit the flask with a thermometer reading from 145 to 200° C. in such a way that the mercury bulb shall be opposite the side tube of the flask and the 175° mark below the cork. Place 100 cc. of the turpentine to be examined in the flask, connect with the condenser, insert stopper bearing thermometer, and heat until distillation of the turpentine begins. Conduct the distillation so that the distillate passes over at the rate of 2 drops per second. Note the initial distilling temperature and the percentage distilling below 170° C.

**Polymerization.** Place 20 cc. of exactly 38/N (100.92 per cent.) sulphuric acid in a graduated, narrow-neck Babcock flask, stoppered, and place in ice-water and cool. Add slowly 5 cc. of the turpentine to be tested. Gradually mix the contents, cooling from time to time, and not allowing the temperature to rise above about 60° C. When the mixture no longer warms up on shaking, agitate thoroughly and place the bottle in a water bath and heat from 60 to 65° C. for about ten minutes, keeping the contents of the flask thoroughly mixed by vigorous shaking five or six times during the period. Do not stopper the flask after the turpentine has been added, as it may explode. Cool to room temperature, fill the flask with concentrated sulphuric acid until the unpolymerized oil rises into the graduated neck. Centrifuge at about 1200 R.P.M. from four to five minutes, allow to stand for twelve hours. Read unpolymerized residue, notice its consistency and color, and determine its refractive index.

<sup>1</sup> Stillman, "Engineering Chemistry," p. 503.

<sup>2</sup> 4% free SO<sub>2</sub>.

### Standards for Turpentine, A. S. T. M.

Turpentine should be clear and free from suspended matter and water, and should conform to the following requirements:

The color shall be "Standard"<sup>1</sup> or better.

The specific gravity shall be not less than 0.862 nor more than 0.872 at 15°.5 C.

The refractive index at 15°.5 C. shall be not less than 1.468 nor more than 1.478.

The initial boiling-point shall be not less than 150 nor more than 160° C.

Ninety per cent of the turpentine shall distill below 170° C.

The polymerization residue shall not exceed 2% and its refractive index at 15°.5 C. shall not be less than 1.500.

### ANALYSIS OF VARNISH

The testing of varnish should largely be of a physical nature. Such properties as odor, consistency, clarity, flowing, time of drying, character of finish, hardness, resistance to moisture and abrasion, elasticity, etc., point out the real value of a varnish. Chemical tests that give additional information, sometimes of a valuable nature, are as follows: Flash point, acid number, ash, character of solvent, fixed oil and resins.

**Flash Point.** A nickel or iron crucible of 60 mm. diameter and 40 mm. height is filled with the varnish to within 20 mm. of the top. It is then supported in a water bath in such a manner as to be about two-thirds immersed in the water. The water should be from 15° to 20° C. at the start and should be heated slowly so that the temperature of the varnish, as indicated by a thermometer suspended in it, will show a rise of about 1 degree per minute. Test for flash at each half degree, using a very small flame.

**Acid Number.** Ten to 20 grams of the varnish are weighed into a small Erlenmeyer flask, 50 cc. neutral alcohol added, and a small funnel inserted in the neck. Heat on the water bath for one-half hour, with occasional shaking. Allow to cool somewhat, add two drops of phenolphthalein indicator and titrate with tenth-normal potassium hydroxide solution. The acid number is the number of milligrams of KOH required to neutralize each gram of the varnish.

**Ash.** Weigh in a porcelain or fused silica crucible several grams of the varnish. Burn off over a small Bunsen flame, using great caution to avoid boiling over and spattering. When all combustible matter is destroyed, weigh the ash and if desired analyze it.

**Solvent.** Steam distillation of a portion of the varnish will remove the solvents, leaving a residue of fixed oils and varnish resins, which may be weighed after driving off the water. The distillate should be examined as recommended under Methods for the Examination of Turpentine. The amount of mineral spirits and turpentine may thus be determined.

**Fixed Oils and Resins.** In the above determination, the total amount of fixed oils and resins is obtained. It is a difficult matter, however, to determine the exact

<sup>1</sup> The term "Standard" refers to the color recognized as standard by the "Naval Stores Trade." Turpentine is of "Standard" color when a depth of 50 mm. in a perfectly flat polished bottom tube, approximately matches a No. 1 yellow Lovibond glass.

percentage and character of resins that have been used in the manufacture of the varnish. This is due to the fact that during the process of heating oils in the presence of resins many intricate chemical changes are brought about, a considerable portion of the resins being distilled off in the form of vapors and combinations of the oil brought about that are difficult of separation. One of the best methods, however, of separating the fixed oils and varnish resins is carried out in the following manner.

- A portion of about a half ounce of the varnish resin should be placed in a 300-cc. tared beaker. There should then be added about 200 cc. of ice-cold petroleum ether and the beaker should be covered and allowed to stand, preferably in a dish containing ice. In an hour's time the resinous ingredients will be found precipitated at the bottom of the beaker or adhering to the side thereof (with the exception of rosin, which is largely soluble in petroleum ether). The precipitated resins should be washed with fresh portions of cold petroleum ether two or three times, pouring the decanted portions into a large bottle. The combined portions of petroleum ether may then be filtered through a tared filter, adding by the aid of a stirring rod the resins contained in the beaker. The filter paper and the beaker with the resins may then be dried at 100° C. and weighed. The combined filtrates may be distilled to obtain the fixed oil which may be examined for constants. (This fixed oil may contain rosin.) The amount of rosin contained in a varnish may be roughly ascertained by thoroughly shaking in a separatory funnel a portion of the varnish with a large quantity of absolute alcohol. The rosin may be obtained by evaporation of the alcoholic extracts. The fixed oils after oxidation or polymerization, as caused by the heating of the varnish during manufacture, are not readily soluble in alcohol.

**Separation of Polymerized Oils and Resins.** In the making of varnish, some oils become oxidized or polymerized to a condition resembling resins. For instance, when a varnish is examined for resins by the above method, it will often be found that a considerable amount of matter insoluble in petroleum ether will be obtained even when hard resins are absent. The insoluble substance is oxidized or polymerized oil. It may be differentiated from varnish resins by the fact that it is readily saponified by alcoholic potash. The following method by Boughton (Technologic Paper No. 65, U. S. Bureau of Standards), though involving considerable work, is probably the most accurate method for the separation of polymerized oils and resins.

To about 4 grams of varnish in a flask add about 25 cc. of water and boil until the volume is about 10 cc. This removes nearly all of the volatile. Add 25 cc. half normal alcoholic potash and 25 cc. benzol and boil under a reflux condenser for one-half hour. Evaporate the solution to about 15 cc. and add about 10 cc. of alcohol. Transfer completely to a separatory funnel, washing the flask with water and ether and using a policeman if necessary. Dilute with water to about 100 cc., add 100 cc. of ether, and shake. Add a few cc. of alcohol if necessary to make the layers separate. Draw off the aqueous layer and wash the ether three times with water and transfer to a tared flask for future use.

To the combined soap solution and washings, add an excess of hydrochloric acid and extract twice with 50 cc. of ether. Discard the aqueous layer, wash the combined ether extracts with water, transfer to a flask and distill off the ether. To the dry residue add 20 cc. of absolute alcohol and 20 cc. of a mixture of 1 volume of sulphuric acid and 4 volumes of absolute alcohol and boil for two minutes under a reflux condenser. Completely transfer the contents of the flask

to a separatory funnel, washing the flask with water and ether. Add 100 cc. ether and after agitation add 100 cc. of 10 per cent sodium chloride solution and again shake. Draw off the aqueous layer, extract it with 50 cc. of ether, combine the ether solutions and wash with water. Add 50 cc. of a fifth-normal potassium hydroxide solution and 10 cc. of alcohol, shake and draw off the lower layer into a second funnel. Wash the ether layer with 50 cc. of water containing 5 cc. of the potassium hydroxide solution and 5 cc. of alcohol.

Extract the combined aqueous portions with two 50 cc. portions of ether and finally wash the combined ether solutions (containing the ethyl esters of the fatty acids) with water.

Distill off the ether and boil the residue with 25 cc. of half-normal alcoholic potash for one-half hour under a reflux condenser. Transfer completely to a separatory funnel and extract the soap four times with ether. Wash the combined ether solution twice with water and add it to the first ether solution of unsaponifiable matter obtained.

Unite the solution and washings containing the soaps, add an excess of hydrochloric acid, and extract twice with ether. Transfer to a tared flask the combined ether solutions, after washing them with water, distill off the ether, dry the residue to constant weight at 110° C. and weigh as "fatty acids."

Report the percentage of fatty acids as percentage of oil and calculate the percentage of resin by difference.

## OTHER MATERIALS

For detailed methods other than those given in this work, for the examination of shellac, resins, bitumens and other raw materials of the vehicle portion of paints and varnishes, the following references may be consulted:

Proceedings of the American Society for Testing Materials (Committee D-1), 1910-15.

Analysis of Paints and Varnishes. Gardner and Schaeffer. McGraw-Hill Book Co., New York.

Manufacture of Varnishes. Livache and McIntosh. Vols. I-III. Scott Greenwood & Son, London.

*Japan Driers, Shellac and Shellac Varnishes:*

Griffin Technical Methods of Analysis, McGraw-Hill Book Company, New York, N. Y.

Report of the Sub-committee on Shellac Analysis, J. Amer. Chem. Soc., 29, 1221 (1907).

*Hexabromide Test for Linseed Oil:*

Proceedings of the A. S. T. M., 1920, 20, Part 1, p. 396.

*Browne Heat Test for Tung Oil (Revised):*

Proceedings of the A. S. T. M., 1920, 20, Part 1, p. 819.

*Turpentine:*

Proceedings of the A. S. T. M., 1920, 20, Part 1, p. 680.

*General:*

Proceedings of the American Society for Testing Materials (Committee D-1), 1910-1920.

Analysis of Paints and Varnishes. Gardner and Schaeffer. McGraw-Hill Book Co., New York.

Interdepartmental Committee on Paint Specification Standardization. Published as Circulars by the United States Bureau of Standards, Washington, D. C.

Composite Thinner, Circular No. 102.

Turpentine, Circular No. 86.

Liquid Paint Drier, Circular No. 105.

Spar Varnish,<sup>1</sup> Circular No. 103.

Asphalt Varnish, Circular No. 104.

Volatile Mineral Spirits, Circular No. 98.

Linseed Oil, Circular No. 82.

A revision of this circular is in preparation.

## THE ANALYSIS OF PAINT PIGMENTS

The vehicle having been extracted from the paint under examination, by the previously outlined methods, the pigment is left ready for analysis. The pigment can be readily classified under one of the following heads by its color, thus shortening any preliminary examination. Many of the colors have a white base which necessitates a determination of both the colored portion of the pigment and any white base which may have been used.

The general analysis of colored pigments is carried out according to the specific method outlined for the individual colored pigments, together with the methods for a composite white paint, provided a qualitative examination does not directly reveal the identity of the pigment.

The pigments used in the manufacture of paints are classified as follows, in certain instances the trade names being given by which the particular pigments are known.

### White Pigments

#### Lead Pigments

Sublimed White Lead—Basic Sulphate of Lead—Basic Sulphate—White Lead.

Corroded White Lead—Basic Carbonate of Lead.

Old Dutch Process White Lead.

Quick Process White Lead.

Mild Process White Lead.

Zinc Lead.

Leaded Zinc.

#### Zinc Pigments

Zinc Oxide—Zinc White.

Lithopone—Ponolith—Beckton White—Charlton White—Orr's White.

#### Silica Pigments

Silica—Silex.

Asbestine—Talcose.

China Clay—Kaolin—Tolamite.

#### Calcium Pigments

Whiting—Paris White—Chalk—Alba Whiting—Spanish White.

Gypsum—Plaster of Paris—Terra Alba—Agalite.

#### Barium Pigments

Barytes—Barite—Blanc Fixe—Barium Sulphate.

Barium Carbonate—Witherite.

### Red and Brown Pigments

Red Lead—Orange Mineral.

Vermilion.

Ochres—Tuscan Red—Indian Red—Venetian Red.

Umbers—Siennas.



**Blue Pigments**

Sublimed Blue Lead.  
 Ultramarine Blue.  
 Prussian Blue—Antwerp Blue—Chinese Blue.

**Yellow and Orange Pigments**

Chrome Yellow—Lemon Yellow—Medium Chrome Yellow.  
 American Vermilion—Orange Chrome—Basic Lead Chromate.  
 Orange Mineral.

**Green Pigments**

Chrome Green.  
 Chromium Oxide.  
 Green Earth.

**Black Pigments**

Graphite.  
 Carbon Black—Bone Black—Lamp Black—Drop Black—Ivory Black—Mineral Black.  
 Willow Charcoal.  
 Black Oxide of Iron.

**ANALYSIS OF WHITE PIGMENTS****SUBLIMED WHITE LEAD****Basic Sulphate of Lead. Basic Sulphate—White Lead**

This pigment, embracing the daily analysis by the manufacturers of the product of over five months' time, shows the following average composition:

Lead sulphate .....	76.68%
Lead oxide.....	17.23
Zinc oxide.....	5.79
	<hr/>
	99.70

The remaining .3 of 1 per cent consists of moisture and ash which are rarely determined.

The analysis of this pigment based on the following method,<sup>1</sup> which depends upon the above average composition, together with the volumetric determination of the total lead and zinc contents, is rapid and accurate.

<sup>1</sup> Jour. of Ind. and Eng. Chem., 6, 3, 200, March, 1914.

**Volumetric Determination of Lead<sup>1</sup>**

One gram of the sample is dissolved in 100 cc. of an acid ammonium acetate solution made up as follows:

Eighty per cent acetic acid.....	125 cc.
Concentrated ammonium hydroxide.....	95 cc.
Water.....	100 cc.

Add this solution hot, dilute with 50 cc. water and boil until a clear solution is obtained. Dilute to 200 cc. and titrate with standard ammonium molybdate solution, using a freshly prepared solution of tannic acid as an outside indicator.

A solution of ammonium molybdate containing 8.67 grams per liter usually gives a solution where,

One cc. = 0.01 gram Pb.

Standardize against pure PbO, pure PbSO<sub>4</sub>, or clean lead foil.

For further details of this method see p. 239.

**Volumetric Determination of Zinc<sup>2</sup>**

Boil 1 gram of the sample with the following solution:

Water.....	30 cc.
Ammonium chloride.....	4 grams
Concentrated hydrochloric acid.....	6 cc.

If the sample is not quite dissolved, the result is unaffected, as the residue is lead sulphate or precipitated lead chloride.

Dilute to 200 cc. with hot water. Add 2 cc. of a saturated sodium hypsulphite solution and titrate with a standard solution of potassium ferrocyanide, using a 5% solution of uranium nitrate as an outside indicator. Calculate the zinc to zinc oxide.

Using the average total of 99.70%, the total lead found and the zinc oxide content, the composition of this pigment is determined by the following calculation:

Total percentage of lead compounds present  
 = total percentage found of ZnO, PbO and PbSO<sub>4</sub> - percentage of ZnO.  
 Total percentage of lead compounds present  
 = 99.70% (average total) - percentage ZnO.

Atomic weight lead..	207.1
Molecular weight lead oxide.....	223.1
Molecular weight lead sulphate.....	303.1

As a hypothetical case, we can assume the presence of a 4.70% ZnO and 99.00% metallic lead.

<sup>1</sup> Modification of Low's Method, "Technical Methods of Ore Analysis," p. 149.

<sup>2</sup> Low's Method, "Technical Methods of Ore Analysis," p. 284.

$$\frac{\left(\frac{\text{Mol. wt. PbSO}_4}{\text{At. wt. Pb}} \times \% \text{ Pb found}\right) - \% \text{ Pb constituents}}{\frac{\text{Mol. wt. PbSO}_4 - \text{mol. wt. PbO}}{\text{Mol. wt. PbO}}} = \% \text{ PbO present}$$

$$\frac{\left(\frac{\text{Mol. wt. PbO}}{\text{At. wt. Pb}} \times \% \text{ Pb found}\right) - \% \text{ Pb constituents}}{\frac{\text{Mol. wt. PbO} - \text{Mol. wt. PbSO}_4}{\text{Mol. wt. PbSO}_4}} = \% \text{ PbSO}_4 \text{ present.}$$

Determining the percentage of lead oxide and lead sulphate present by the above formulas we find:

$$\frac{\left(\frac{303.1}{207.1} \times 69.00\right) - 95.00}{\frac{303.1 - 223.1}{223.1}} = \text{per cent PbO} = 16.68$$

$$\frac{\left(\frac{223.1}{207.1} \times 69.00\right) - 95.00}{\frac{223.1 - 303.1}{303.1}} = \text{per cent PbSO}_4 = 78.32.$$

If it is necessary actually to determine the percentage of lead sulphate present, the following procedure may be followed:

#### Total Sulphate

Mix 0.5 gram of the sample with 3 grams of sodium carbonate. Add 30 cc. of water and boil gently for ten minutes. Allow to stand for four hours. Dilute with hot water, filter and wash thoroughly. All the lead sulphate is here changed to lead carbonate, the sodium carbonate being transposed to sodium sulphate, which is found in the filtrate.

The sulphate is determined in the filtrate by precipitation as BaSO<sub>4</sub>. Calculate the BaSO<sub>4</sub> to PbSO<sub>4</sub>. Determine the total lead as above outlined, deduct the lead found as PbSO<sub>4</sub> and calculate the residual lead to PbO.

The foregoing method is the one generally used in the commercial estimation of lead and yields excellent results to the analyst who is familiar with it. However, in laboratories where only occasional lead determinations are made, the well-known gravimetric methods for lead and zinc will sometimes be found preferable. The time required for gravimetric determinations is not much greater and the chance of error is reduced.

The method referred to consists in weighing the lead as sulphate<sup>1</sup> and the precipitation of the zinc from the filtrate with sodium carbonate, igniting it, and weighing as zinc oxide.

<sup>1</sup> As outlined under Basic Carbonate of Lead, p. 625.

## CORRODED WHITE LEAD

Basic Carbonate of Lead<sup>1</sup>—Old Dutch Process White Lead—Quick Process White Lead—Mild Process White Lead

Corroded white lead contains approximately 80% metallic lead and 20% carbonic acid and combined water with traces sometimes of silver, antimony and other metals. The formula for this compound is  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ .

## Total Lead (Gravimetric)

Dissolve 1 gram in 20 cc. of  $\text{HNO}_3$  (1:1) in a covered beaker, heating till all  $\text{CO}_2$  is expelled; wash off cover, add 20 cc. of  $\text{H}_2\text{SO}_4$  (1:1) and evaporate to fumes of  $\text{SO}_3$ , cool, add about 150 cc. of water and 150 cc. of ethyl alcohol; let stand in cold water one hour, filter on a Gooch crucible, wash with 95% ethyl alcohol, dry at  $110^\circ \text{C}$ ., and weigh the  $\text{PbSO}_4$ . Calculate to  $\text{PbO}$  or to basic carbonate.<sup>2</sup> Instead of determining the lead as sulphate, the sample may be dissolved by boiling with acetic acid; then dilute to about 200 cc. with water, make alkaline with  $\text{NH}_4\text{OH}$ , then acid with acetic acid, heat to boiling and add 10 to 15 cc. of a 10% solution of potassium dichromate; heat till the yellow precipitate assumes an orange color. Let settle and filter on a Gooch crucible, washing by decantation with hot water till the washings are colorless, finally transferring all of the precipitate. Then wash with 95% ethyl alcohol and then ether; dry at  $110^\circ \text{C}$ . and weigh  $\text{PbCrO}_4$ . (Any insoluble matter should be filtered out before precipitating the lead.)

## Total Lead (Volumetric)

Dissolve 0.5 gram of sample in 10 cc. of concentrated hydrochloric acid, boil till solution is effected, cool, dilute to 40 cc. and neutralize with ammonium hydroxide. Add acetic acid until distinctly acid, dilute to 200 cc. with hot water, boil and titrate with ammonium molybdate as follows:

Dissolve 4.25 gram of ammonium molybdate in water and make up to one liter. To standardize this solution, dissolve about 0.2 gram of pure lead foil in nitric acid (pure  $\text{PbO}$  or  $\text{PbSO}_4$  may also be used), evaporate nearly to dryness, add 30 cc. of water, then 5 cc.  $\text{H}_2\text{SO}_4$  (sp.gr. 1.84), cool, and filter.

Drop filter with  $\text{PbSO}_4$  into a flask, add 10 cc. concentrated  $\text{HCl}$ , boil till completely disintegrated, add 15 cc. of  $\text{HCl}$ , 25 cc. of water, and  $\text{NH}_4\text{OH}$  till alkaline. Acidify with acetic acid, dilute to 200 cc. with hot water and boil. Titrate, using an outside indicator of one part of tannic acid in 300 parts of water.

It should be noted that when calcium is present, it forms a more or less insoluble molybdate, and results are apt to be high. With samples containing less than 10% of lead, the lead should be precipitated as  $\text{PbSO}_4$ , filtered, redissolved and titrated as in the process of standardizing.

## Carbon Dioxide

Determine by evolution with dilute hydrochloric acid absorbing in soda-lime or  $\text{KOH}$  solution. Calculate  $\text{CO}_2$  to  $\text{PbCO}_3$ , subtract  $\text{PbO}$  equivalent from total  $\text{PbO}$  and calculate residual  $\text{PbO}$  to  $\text{Pb(OH)}_2$ .

<sup>1</sup>Tentative Methods for the Routine Analysis of White Pigments. Report of Commission D-1, American Society for Testing Materials, 1915.

<sup>2</sup>This method of weighing lead sulphate is not accurate in the presence of calcium compounds.

### Acetic Acid<sup>1</sup>

Place 18 grams of the pigment in a 500-cc. flask, add 40 cc. of sirupy phosphoric acid, 18 grams of zinc dust and 50 cc. of water. Connect to a straight Liebig condenser, apply heat and distill down to a small bulk. Then pass steam into the flask until it becomes about half full of condensed water, shut off the steam and distill down to a small bulk—this operation being conducted twice. To the total distillate which was collected in a larger flask add 1 cc. of sirupy phosphoric acid, connect to a Liebig condenser, using a spray trap, and distill to a small volume—about 20 cc. Pass steam through till about 200 cc. of water condense in the distillation flask, shut off steam and continue the distillation. These operations of direct and steam distillations are conducted until 10 cc. of the distillate require only 1 drop of 0.1 N alkali to give a change in the presence of phenolphthalein. Then titrate the total distillate with 0.1 N sodium hydroxide and phenolphthalein and calculate the total acidity as acetic acid. It will be found convenient to titrate each 200-cc. portion of the distillate as collected.

### Metallic Lead<sup>1</sup>

Weigh 50 grams of the sample into a 400-cc. beaker, add a little water and add slowly 60 cc. of 40% acetic acid and after effervescence has ceased, boil on hot plate. Fill the beaker with water, let settle, and decant the clear solution. To the residue add 100 cc. of a mixture of 360 cc. of strong  $\text{NH}_4\text{OH}$ , 1080 cc. of water, 2160 cc. of 80% acetic acid, and boil until all solution is complete. Fill the beaker with water, let settle and decant the clear solution. Collect residue on a watch-glass, floating off everything but metallic lead. Dry and weigh. Result  $\times 2$  = percentage of metallic lead in sample.

The following method of A. N. Finn (unpublished) gives total basicity of a pure white lead: Place 2 grams of pigment in an evolution flask, add a little  $\text{CO}_2$ -free water, connect with a separatory funnel and condenser (Knorr type), add through the funnel, finally washing down, 100 cc. of N/4 nitric acid, boil and absorb the  $\text{CO}_2$  in a soda lime tube in the usual manner (having  $\text{H}_2\text{SO}_4$  and  $\text{CaCl}_2$  drying tubes in train) and weigh. To the solution in the evolution flask, add about 20 cc. of neutral sodium sulphate solution and titrate with N/4 sodium hydroxide solution (carbonate-free), using phenolphthalein.  $\text{CO}_2$  is calculated to  $\text{PbCO}_3$ . The amount of N/4 acid corresponding to the  $\text{CO}_2$  is calculated and deducted from the total amount of N/4 acid neutralized by the sample and the difference calculated to combined  $\text{H}_2\text{O}$ , from which  $\text{Pb(OH)}_2$  is computed.

### ZINC LEAD AND LEADED ZINC

Zinc lead and leaded zinc are varying compounds containing zinc oxide and lead sulphate, the former showing approximately 50% zinc oxide and 50% lead sulphate, while the latter contains on an average 25% lead sulphate and 75% zinc oxide. See also pp. 277, 600, Vol. I.

These pigments may be analyzed by the following procedure:

**Moisture.** Heat 2 grams at  $105^\circ \text{C}$ . for two hours.

<sup>1</sup> Thompson's Method, Jour. Soc. Chem. Ind., 24, 487 1905.

**Lead and Zinc.** Determine the lead directly by the volumetric molybdate method and the zinc by the volumetric ferrocyanide method as outlined under Sublimed White Lead. See also pages 277 and 600, Vol. I.

**Total Soluble Sulphates<sup>1</sup>** (in the absence of  $\text{BaSO}_4$ ). Treat 0.5 gram of the sample with 5 cc. of water, 3 grams of  $\text{NH}_4\text{Cl}$  and 5 cc. of  $\text{HCl}$  saturated with bromine; digest (covered) on the steam bath about fifteen minutes, add 25 cc. of  $\text{H}_2\text{O}$ , neutralize with dry  $\text{Na}_2\text{CO}_3$  and add about 2 grams more. Boil ten to fifteen minutes; let settle, dilute with hot water, filter and wash with hot water; redissolve in  $\text{HCl}$ , reprecipitate as above and wash thoroughly with hot water. Acidify the united filtrates with  $\text{HCl}$  and add a slight excess of 10%  $\text{BaCl}_2$  solution. Let stand on steam bath for one hour, filter, wash with hot water, ignite and weigh the  $\text{BaSO}_4$ . Calculate to  $\text{SO}_3$  (includes  $\text{SO}_3$  formed from  $\text{SO}_2$ ).

**Total Soluble Sulphate** (in the presence of  $\text{BaSO}_4$ ). Treat 1 gram in a 600-cc. beaker with 10 cc. of  $\text{H}_2\text{O}$ , 10 cc. of strong  $\text{HCl}$ , saturated with bromine, and 5 grams of  $\text{NH}_4\text{Cl}$ , heat on a steam bath in a covered beaker for five minutes, add hot water to make about 400 cc., boil for five minutes and filter to separate any insoluble material. (A pure pigment should be completely dissolved.) Wash with hot water, ignite and weigh the insoluble. Remove lead with  $\text{Na}_2\text{CO}_3$  as above, making a double precipitation, acidify, and to the boiling hot filtrate add slowly, with stirring, 20 cc. of a 10%  $\text{BaCl}_2$  solution; let stand for two hours on the steam bath, filter, wash, ignite, and weigh as  $\text{BaSO}_4$ . (Includes  $\text{SO}_3$  formed from  $\text{SO}_2$ .)

**Soluble Zinc Sulphate.** Boil 2 grams of the sample with 150 cc. of water and 50 cc. of alcohol for thirty minutes, filter and wash with a mixture of alcohol and water (1:3). Heat the filtrate to boiling and expel most of the alcohol; then determine  $\text{SO}_3$  by the usual method of precipitation with  $\text{BaCl}_2$ . Calculate to  $\text{ZnSO}_4$  and to  $\text{SO}_3$ .

**Sulphur Dioxide.** Digest 2 grams of the sample with frequent stirring in 100 cc. of freshly boiled cold water and 5 cc. of concentrated  $\text{HCl}$ ; let stand ten to fifteen minutes, add an excess of 0.01 normal iodine solution and titrate back with 0.01 normal sodium thiosulphate solution, using starch indicator. Report as  $\text{SO}_2$ . Run blank on reagents and make corrections.

**Calculations.** Report soluble  $\text{SO}_3$  as  $\text{ZnSO}_4$ . Deduct  $\text{ZnO}$  equivalent of the  $\text{ZnSO}_4$  from total  $\text{ZnO}$  and report residue as  $\text{ZnO}$ . Deduct soluble  $\text{SO}_2$  and  $\text{SO}_3$  equivalent to  $\text{SO}_2$  from total  $\text{SO}_3$ , calculate remainder to  $\text{PbSO}_4$ ; subtract  $\text{PbO}$  equivalent of  $\text{PbSO}_4$  from total  $\text{PbO}$  and report remainder as  $\text{PbO}$ .

## ZINC OXIDE<sup>2</sup>

**Moisture.** Weigh 10 grams on watch-glass and dry for two hours at 105 to 110° C. Cool and weigh.

**Carbon Dioxide.** Place 10 grams in a 4-ounce Erlenmeyer flask, moisten with water, add solution of  $\text{KMnO}_4$  to oxidize  $\text{SO}_2$ , insert a two-hole rubber stopper, with an acid delivery tube and connect to a carbon dioxide apparatus. This apparatus consists of a tube containing  $\text{KOH}$  solution, preceding the flask with

<sup>1</sup> Report of Sub-committee VIII of Committee D-1, Proceedings of American Society for Testing Materials, 14, 271-2, 1914.

<sup>2</sup> Frank G. Breyer, Chief, Testing Department, The New Jersey Zinc Co.

sample, to absorb any  $\text{CO}_2$  from the air drawn in. The flask is followed by a tube with concentrated  $\text{H}_2\text{SO}_4$  to absorb moisture, a calcium chloride tube, and next is a weighed Geissler <sup>1</sup> bulb with KOH solution, to absorb the  $\text{CO}_2$  from the sample; this is followed by another calcium chloride tube which is connected to a suction line. The acid delivery tube contains 25 cc.  $\text{H}_2\text{SO}_4$  (1 : 1) and before opening the stopcock the suction is applied to insure that the connections are all air-tight; if there is no leak the acid is allowed to flow into the flask and the suction regulated so that the bubbles in the Geissler bulb may easily be counted. The flask is heated cautiously to boiling for a minute or two, the flame removed and the suction allowed to proceed from thirty to forty minutes. The Geissler <sup>1</sup> bulb is then disconnected, placed in the balance for fifteen minutes together with the end calcium chloride tube and then weighed. The KOH solution used for absorption is of the same strength as for carbon in steel.

**Insoluble.** Treat 10 grams in a 250-cc. beaker with 50 cc. concentrated HCl, evaporate to dryness, take up residue with HCl and water, filter and wash thoroughly with HCl (1 : 4) and hot water. Ignite filter paper and contents in a weighed platinum crucible.

**Sulphuric Anhydride; Total S as  $\text{SO}_3$ .** Treat 10 grams with 50 cc. strong HCl and a few cc. of bromine water; boil to expel bromine, filter from insoluble, wash with hot water. Neutralize the excess of HCl with ammonia, keeping the solution slightly acid, heat to boiling and add about 15 cc. of hot  $\text{BaCl}_2$ . Let stand overnight, filter on a weighed Gooch crucible, wash well with hot water, ignite in a muffle, cool and weigh as  $\text{BaSO}_4$ .

### Lead Oxide

**Gravimetric Method.** Treat 10 grams with 50 cc. strong HCl and 50 cc.  $\text{H}_2\text{SO}_4$  (1 : 1), evaporate on a hot plate, and finally over a Bunsen burner to strong fumes of  $\text{SO}_3$ .

Cool, and add 100 cc. water, heat again to dissolve the soluble sulphates, cool, add 25 cc. 95% alcohol, let stand overnight, filter on a Gooch crucible and wash with dilute  $\text{H}_2\text{SO}_4$ , and finally with alcohol. Dry at  $110^\circ\text{C}$ ., ignite for five to ten minutes, cool and weigh. Dissolve the  $\text{PbSO}_4$  in the Gooch crucible with a hot solution of ammonium acetate, slightly acidify with acetic acid, wash with hot water, dry at  $110^\circ\text{C}$ ., ignite and weigh again. The loss in weight is  $\text{PbSO}_4$ , from which the  $\text{PbO}$  is calculated.

**Electrolytic Method.** 9.330 grams of the sample are dissolved in a 250-cc. beaker with 40 cc. concentrated  $\text{HNO}_3$  and about 50 cc. of distilled water. The solution is boiled for a few minutes until all red fumes are expelled. Add enough silver nitrate solution to precipitate all chlorides (an excess of silver nitrate does not interfere) and dilute to about 200 cc.

Electrolyze for two hours, using about .5 ampere current. The solutions are tested for lead before turning off the current by raising the liquid in the beaker, and allowing to continue for twenty minutes. If there is no fresh deposit of  $\text{PbO}_2$ , the electrode is washed three times with distilled water (current still on) and then after removal from the electrolytic stand, with alcohol. After drying one hour at  $110^\circ\text{C}$ . the electrode is weighed. The weight of  $\text{PbO}_2$  in milligrams divided by 100 gives the percentage of  $\text{PbO}$ .

<sup>1</sup>See Procedure for  $\text{CO}_2$  determination in the chapter on Carbon, p. 103.

**Chlorine.** Treat 10 grams of sample with 50 cc. strong  $\text{HNO}_3$ , add 10 cc.  $\text{N}/10 \text{ AgNO}_3$ , boil, cool, add 10 cc. ferric nitrate (1 : 3), and titrate the excess of  $\text{AgNO}_3$  with  $\text{NH}_4\text{CNS}$  (9 grams per liter of solution). A blank determination is conducted in a similar manner and from the amount of  $\text{N}/10 \text{ AgNO}_3$  required the chlorine is calculated.

**Ferric Oxide.** Treat 10 grams with 50 cc. strong  $\text{HCl}$ , add about 1 gram  $\text{KClO}_3$ , and boil down to a syrupy consistency. Cool, add water and a large excess of ammonia. Allow to stand until the ferric oxide separates, and filter; wash with dilute ammonia water and then with hot water. Dissolve the precipitate of ferric oxide in an Erlenmeyer flask with warm dilute  $\text{H}_2\text{SO}_4$ . Wash the filter paper thoroughly with hot water, dilute the solution in the Erlenmeyer flask to about 200 cc. and pass in hydrogen sulphide for five minutes. Place a funnel in the neck of the flask and boil until all  $\text{H}_2\text{S}$  is expelled. Cool and titrate with dilute  $\text{KMnO}_4$ . A blank determination is carried out in a similar manner and the number of cc. of  $\text{KMnO}_4$  required to give a pink color is subtracted from the total number required on the sample.

**Manganese Oxide.** Treat a 10-gram sample in a 16-oz. Erlenmeyer flask with 100 cc. of  $\text{HNO}_3$  (1 : 3), heat to boiling and add a pinch of sodium bismuthate, when the pink color of permanganic acid is produced; now add a few cc. of dilute  $\text{Na}_2\text{S}_2\text{O}_3$  solution to destroy the pink color, and continue boiling to drive off all nitrous oxide fumes. Cool thoroughly and add 50 cc. of a 3% solution of  $\text{HNO}_3$ , and a very small pinch of sodium bismuthate to restore the pink color again. Filter the solution through a Gooch crucible to remove the excess of sodium bismuthate, rinsing the flask and Gooch with 50 cc. of 3%  $\text{HNO}_3$  solution to which a small amount of sodium bismuthate has been added. Now add 10 cc. of ammonium ferrous sulphate solution, and titrate the excess of ammonium ferrous sulphate with standard  $\text{KMnO}_4$  whose iron value has been determined. One gram of  $\text{KMnO}_4$  per liter is a convenient strength; and 12.4 grams of ammonium ferrous sulphate, and 50 cc. strong  $\text{H}_2\text{SO}_4$  to the liter gives a solution which is almost equal to the permanganate solution. A blank determination is carried out in exactly the same manner as with the sample of oxide, and the difference in the number of cc. of  $\text{KMnO}_4$  required to give a pink color with the blank determination and the sample of oxide is equal to the amount of  $\text{MnO}$  present. The manganese value of the  $\text{KMnO}_4$  is calculated from the iron value, according to the ratio of  $\text{Mn} : \text{Fe}$ , or 55 : 279.5 or 0.1968 : 1.

**Arsenous Oxide.** Weigh 10 grams of oxide in a 16-ounce Erlenmeyer flask, add about 10 grams of  $\text{FeSO}_4$ , place a rubber stopper with an acid delivery tube and an exit tube, which is immersed in a beaker containing about 200 cc. distilled water. The beaker of water is placed in a pan of cold water, the pan having an inlet and overflow. Now add 100 cc. strong  $\text{HCl}$  from the delivery tube, and heat the flask to boiling so as to distill the arsenic into the beaker of water. Continue boiling until about two-thirds of the acid has been distilled, remove from the flame, rinse the delivery tube, add 10 cc. strong  $\text{HCl}$  to the solution in the beaker, warm and pass in  $\text{H}_2\text{S}$  to precipitate the arsenic, as  $\text{As}_2\text{S}_3$ . Let stand in a warm place for some time and filter in a Gooch crucible, wash the precipitate of  $\text{As}_2\text{S}_3$  with alcohol and then with carbon bisulphide and several times with dilute alcohol. Dry at  $105^\circ \text{C}$ . for one hour and weigh. Dissolve the  $\text{As}_2\text{S}_3$  in the Gooch crucible with dilute ammonia water, wash well with hot water, and dry at  $105^\circ \text{C}$ . and reweigh. The loss in weight is  $\text{As}_2\text{S}_3$ , from which the  $\text{As}_2\text{O}_3$  may be calculated. See procedure for arsenic distillation, p. 37.



**SO<sub>2</sub> Equivalent.** Treat 10 grams in a 250-cc. beaker with 25 cc. cold water, 25 cc. hot water, add some starch solution and titrate with N/10 iodine solution, gradually adding 25 cc. HCl until a permanent blue color appears.

**Zinc Oxide.** The percentage of ZnO is found by adding together all the percentages of impurities, except the SO<sub>2</sub> equivalent, and subtracting this sum from 100.

### LITHOPONE

#### Ponolith—Beckton White—Charlton White, etc.

This pigment is a chemically precipitated pigment containing approximately from 69 to 70 per cent barium sulphate, the remainder consisting of zinc sulphide, with occasional impurities of zinc oxide and carbonate.

**Moisture.** Heat 2 grams for two hours at 105° C.

**Barium Sulphate.** Treat 1 gram with 10 cc. conc. HCl and 1 gram of potassium chlorate, added in small amounts. Evaporate to one-half its volume, add 100 cc. hot water and a few cc. of dilute H<sub>2</sub>SO<sub>4</sub>. Boil, filter, wash and weigh the insoluble residue, which should show only the presence of barium sulphate. Examine the residue for silica and alumina.

**Total Zinc.** Determine the total zinc in the filtrate by the volumetric method as outlined under Sublimed White Lead.

**Zinc Sulphide.** Digest 1 gram at room temperature for one-half hour with 100 cc. of 1% acetic acid. Filter and determine the zinc in the precipitate by solution in HCl as under Sublimed White Lead.

Zinc soluble in acetic acid is reported as zinc oxide, zinc insoluble as zinc sulphide. The filtrate from the acetic acid treatment, after precipitating the zinc as zinc sulphide and subsequent removal, should be examined for barium which might be present as carbonate, and calcium, present as either sulphate or carbonate. The zinc sulphide may also be determined by the method as outlined under Tentative Methods for Analysis of Pigments by Committee D-I<sup>1</sup> as follows:

**Zinc Sulphide.<sup>2</sup>** Place 0.5 gram of the pigment in an evolution flask<sup>3</sup> with about 10 grams of "feathered" or mossy zinc, add 50 cc. of water; insert the stopper carrying a separatory funnel and an exit tube. Run in 50 cc. of concentrated HCl from the funnel, having previously connected the exit tube to two absorption flasks, in series; first flask contains 100 cc. of alkaline lead nitrate solution, second flask, 50 cc. of same as a safety device. After all of the acid has run into the evolution flask, heat slowly, finally boiling until the first appearance of steam in the first absorption flask. Disconnect, let the lead sulphide settle, filter, wash with cold water, then with hot water till neutral to litmus paper and washings give no test for lead. The PbS precipitate is dissolved in hot, dilute HNO<sub>3</sub>, evaporated to fumes with H<sub>2</sub>SO<sub>4</sub>, and finally weighed as PbSO<sub>4</sub>. Calculate PbS or PbSO<sub>4</sub> to ZnS.

The alkaline lead solution is made as follows: Into 100 cc. of KOH solution (56 grams in 140 cc. of H<sub>2</sub>O) pour a saturated solution of lead nitrate (250 grams in 500 cc. of H<sub>2</sub>O) until the precipitate ceases to redissolve, stirring constantly

<sup>1</sup> American Society for Testing Materials, 1915.

<sup>2</sup> Evolution Method of W. G. Scott, "White Paints and Painting Material," p. 257; see also p. 398, chapter on Sulphur by W. W. Scott.

<sup>3</sup> See Apparatus on p. 399.

while mixing. About three volumes of the lead solution will be required for one of the alkali.

Instead of absorbing the evolved  $H_2S$  in alkaline lead-nitrate solution, a solution of 8 grams of cadmium chloride in 250 cc. of water and 150 cc. of  $NH_4OH$  (sp.gr. 0.90) may be used. The  $CdS$  precipitate may be filtered on a weighed Gooch, washed with water containing a little  $NH_4OH$ , dried at  $100^\circ C.$ , and weighed. Calculate to  $ZnS$ . It is better to filter the  $CdS$  on a small filter and wash as above, then place filter and precipitate in a beaker and dissolve in  $HCl$  and  $KClO_3$  (keeping at room temperature at first). Filter out any paper pulp or insoluble matter, make filtrate alkaline with  $NH_4OH$ , then just acid with  $HCl$ , heat to boiling and precipitate with  $BaCl_2$  in the usual manner. Filter, wash, ignite, and weigh the  $BaSO_4$ . Calculate to  $ZnS$ .

For very rapid work the contents of the absorption flask, after all  $H_2S$  has been absorbed, may be washed into a vessel with cold water and diluted to about 1 liter, acidified with concentrated  $HCl$  and titrated with standard iodine solution, using starch indicator. (The precipitate should be completely dissolved.) The iodine solution is prepared by dissolving about 12.7 grams of pure resublimed iodine and 18 grams of  $KI$  in a little water and then diluting to 1 liter.

**Soluble Salts.** Digest 2 grams with hot water and examine the filtrate for soluble salts.

### SILICA OR SILEX—CHINA CLAY—ASBESTINE

These pigments, while all true silica pigments, are widely different from the standpoint of physical structure. A microscopic examination is of great value, showing silica or silex to consist of small, sharp particles, china clay to be tabloid in appearance and asbestine to consist of long, rod-like fibrous particles.

The following procedure taken from the outlined method published by Subcommittee VIII of Committee D-I<sup>1</sup> will well serve for the analysis of these pigments.

**Moisture.** Heat 2 grams at  $105^\circ$  for two hours.

**Loss on Ignition.** Ignite 1 gram to constant weight in a platinum crucible.

**Insoluble Matter.** Boil 2 grams for thirty minutes with 50 cc.  $HCl$  (1 : 1), add 50 cc. of water, wash, ignite, and weigh insoluble residue.

In the case of China clay, or asbestine, a sodium carbonate fusion should be resorted to, with the subsequent dehydration of the silica.

The insoluble residue in either case is volatilized with  $H_2SO_4$  and  $HF$  in the usual manner, any loss in weight being considered silica. Any residue is fused with sodium carbonate, the fusion being added to the original filtrate. Should  $BaSO_4$  be present, the melt is digested with warm water, the  $BaCO_3$  filtered off, washed, dissolved in hot dilute  $HCl$  and precipitated and determined as  $BaSO_4$ .

The filtrates, combined from the preceding filtrations, are examined for alumina, iron, manganese, calcium and magnesium in the usual way.

Should it be necessary to determine the alkalies present, a separate sample treated according to the method of Mr. J. Lawrence Smith as in Bulletin No. 22, U. S. Geological Survey. See page 416, Vol. I.

**Carbon Dioxide.** Determine by evolution with  $HCl$ , weighing in soda-ash,  $KOH$  solution, or by absorbing in  $Ba(OH)_2$  solution and titrating or weighing as  $BaCO_3$ . See p. 121, Vol. I.

<sup>1</sup> Proceedings of American Society for Testing Materials, 14, 279, 1914.

Any excess of calcium is reported as oxide. The magnesium is calculated as  $MgO$ , unless the carbon dioxide is in excess of the amount of calcium present, in which case it is reported as  $MgCO_3$ , and the remainder as  $MgO$ .

### WHITING—PARIS WHITE

#### Gypsum—Plaster of Paris

These pigments are of the following composition:

**Whiting.** The natural form of calcium carbonate.

**Paris White.** The artificial form of calcium carbonate.

**Gypsum.** The hydrated form of calcium sulphate, of formula  $CaSO_4 \cdot 2H_2O$ .

These pigments are analyzed in the following manner:

**Moisture.** Heat 2 grams at  $105^\circ C$ . for two hours.

**Loss on Ignition.** Ignite 1 gram at a high heat to constant weight. The loss will be water, if carbonates are absent.

**Calcium.** Treat 1 gram with dilute  $HCl$  and a few drops of  $HNO_3$ . Evaporate to dryness, dehydrate, moisten with a few drops of concentrated  $HCl$ , dilute with hot water and determine the insoluble residue. Examine for  $BaSO_4$ . The residue should consist of silica.

In the filtrate, precipitate and determine the iron hydroxide and aluminum hydroxide in the usual manner. The calcium is precipitated in the boiling ammoniacal filtrate with 30 cc. of saturated ammonium oxalate solution, allowing the solution to boil for one-half hour. A double precipitation is here advisable to remove the last traces of magnesium. The calcium oxalate is filtered off, thoroughly washed and determined volumetrically by the permanganate method, p. 92.

**Magnesium.** Determine in the filtrates after removal of the calcium by precipitation as magnesium ammonium phosphate and ignition to magnesium pyrophosphate in the usual manner, p. 293, Vol. I.

**Carbon Dioxide.** Determine as outlined under Silica.

**Sulphates.** Dissolve 1 gram in concentrated  $HCl$ , remove any insoluble residue, heat to boiling and precipitate any sulphate as  $BaSO_4$ , determining in the usual manner. See p. 497, Vol. I.

### BARYTES AND BLANC FIXE

Of these two barium pigments used in the manufacture of paints, barytes is the natural barium sulphate, while blanc fixe is precipitated barium sulphate. Their barium sulphate content should be not less than 95%.

The following method may be used for the analysis of these pigments:

**Moisture.** Heat 2 grams at  $105^\circ C$ . for two hours.

**Loss on Ignition.** Ignite 1 gram to constant weight. The loss will be reported as loss on ignition, and will consist of free and uncombined water, carbon dioxide and organic matter.

**Barium Sulphate.** Boil 1 gram with dilute  $HCl$ , evaporate to dryness, moisten with  $HCl$ , add water, boil, filter and wash. Should lead be present in the insoluble residue, as shown by the action of  $H_2S$ , treat the insoluble residue with a little (1 : 1)  $HCl$  and several drops of  $H_2SO_4$ . Filter, wash and weigh the residue. Treat the ignited residue with  $H_2SO_4$  and  $HF$ , evaporate to dryness

and ignite. The residue should show no loss as silica. The filtrate is examined for alumina, iron, calcium and magnesium in the usual manner.

**Soluble Sulphates.** Treat 1 gram with 20 cc. conc. HCl, dilute to 200 cc. with hot water, boil, filter, wash, add  $\text{NH}_4\text{OH}$  until neutral, make acid with HCl and precipitate any sulphate as  $\text{BaSO}_4$ . Determine in the usual manner. Calculate to  $\text{CaSO}_4$ . If carbonates are present, calculate the remaining CaO to  $\text{CaCO}_3$ . Any excess of oxide is reported as CaO.

**Carbon Dioxide.** Determine as outlined under silica. If any barium carbonate is present, it is determined in the filtrate from the preliminary HCl treatment, by precipitation and weighing, as  $\text{BaSO}_4$ . Any excess of carbon dioxide over the barium is reported as calcium carbonate.

### ANALYSIS OF A COMPOSITE WHITE PAINT

A white paint may consist of a mixture of any of the preceding pigments, excepting that it is understood that lead pigments and lithopone are seldom found together, owing to their tendency to blacken with the formation of lead sulphide.

After separation from the oil and other liquids as outlined above, the white pigment mixture may be rapidly analyzed by the following method. It is, however, often advisable to resort to a qualitative examination before beginning the quantitative analysis.

**Insoluble Residue.** Boil 1 gram of the sample with 20 cc. (1 : 1) HCl. Evaporate to dryness, moisten the residue with a few cc. of concentrated HCl, allow to stand a few minutes, dilute with hot water, boil, filter and wash the insoluble residue thoroughly with hot water. Treat the insoluble residue with (1 : 1) HCl and 2 cc.  $\text{H}_2\text{SO}_4$  to remove the last traces of lead. Filter, wash and weigh the insoluble residue. Determine the silica by volatilization with  $\text{H}_2\text{SO}_4$  and HF. Any loss is reported as silica. Determine the  $\text{BaSO}_4$  in the residue by boiling with dilute HCl or making a potassium bisulphate fusion. The residue remaining after either of these treatments is reported as barium sulphate.

**Total Lead.** This constituent can be best determined on a separate sample. To 1 gram add 10 cc. of conc.  $\text{HNO}_3$ , boil, add, after cooling, conc.  $\text{H}_2\text{SO}_4$  and evaporate to strong  $\text{SO}_3$  fumes. Dilute with water, allow to stand several hours, filter, wash slightly, dissolve and determine the lead volumetrically as outlined under Sublimed White Lead.

Lead can also be determined on the combined filtrates from the insoluble residue. Precipitate the lead in an acid solution with  $\text{H}_2\text{S}$  and determine volumetrically in the above outlined manner.

To determine whether both sublimed white lead and corroded white lead are present, treat a separate portion of the paint with boiling acetic acid, filter and collect the insoluble residue. Determine the lead either in the filtrate or in the insoluble residue by the volumetric method. The lead soluble in acetic acid is the basic carbonate of lead and the lead oxide from the sublimed white lead, while the lead sulphate from the sublimed white lead remains insoluble.

**Alumina and Iron Oxide.** Remove the  $\text{H}_2\text{S}$  from the filtrate by boiling, after removal of the lead, and precipitate the hydroxides in an ammoniacal solution after boiling with the addition of a few drops of  $\text{HNO}_3$ . Determine and separate in the usual manner.

**Zinc.** Precipitate the zinc in the filtrate from the alumina and iron precipitation, after acidifying with acetic acid, and determine the zinc as outlined under Sublimed White Lead on p. 1179.

**Calcium and Magnesium.** Determine the calcium and magnesium in the filtrate from the precipitation of zinc sulphide in the usual manner, testing, however, first for the presence of barium.

**Sulphate.** Determine as outlined under Zinc Lead and Leaded Zincs.

**Sulphide.** Should lithopone be present, separate the zinc oxide and zinc sulphide as outlined under Lithopone, p. 1186.

**Carbon Dioxide.** Determine as outlined under Silica, p. 1187.

**Calculations.** Silica is reported as silica, except where alumina is present, showing the presence of China clay. In this case, calculate the alumina to clay by the method of Scott.

Weight of  $\text{Al}_2\text{O}_3 \times 2.5372$  = weight of clay.

Weight of clay  $\times 0.4667$  = weight of  $\text{SiO}_2$  in clay.

Any difference greater than 5% may be considered silica.

Barium sulphate is reported as barium sulphate or as lithopone, if zinc sulphide is present, according to the given composition of lithopone, 70% barium sulphate and 30% zinc sulphide.

Lead is reported as Basic Carbonate of Lead on the formula  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ .

Calculate lead soluble in acetic acid, after determining  $\text{CO}_2$  to basic lead carbonate and any residual lead to lead oxide which, together with the lead sulphate is reported as Sublimed White Lead.

Should calcium sulphate be present the portion soluble in water is examined for lime or sulphuric acid and calculated to calcium sulphate, any residual lime being calculated to calcium carbonate and any residual sulphuric acid being calculated to lead sulphate. Any residual  $\text{CO}_2$  after calculating calcium carbonate is calculated to white lead and any residual lead is calculated to lead oxide.

Lead oxide should not be reported except in the presence of lead sulphate. Any large percentage of magnesium denotes the presence of asbestine.

## RED AND BROWN PIGMENTS

These pigments are grouped under these heads:

**The Lead Oxide Pigments—The Iron Oxide and Manganese Oxide Pigments -The Mercury Oxide Pigments**

### RED LEAD AND ORANGE MINERAL

These pigments in the pure form are oxides of lead, of the generally accepted form,  $\text{Pb}_3\text{O}_4$ , being probably mixtures of lead monoxide, and lead dioxide. In chemical composition they are the same, the proportions of lead monoxide and lead dioxide varying, however, but by their physical structure and color they can be readily differentiated.

Two methods are given for the analysis of this pigment. The first is taken from the method as outlined by Sub-committee VIII of Committee D-I.<sup>1</sup>

**Moisture.** Dry 2 grams at  $105^\circ$  for two hours.

<sup>1</sup> Proceedings of American Society for Testing Materials, 14, 281-283, 1914.

**Organic Color.** Boil 2 grams with 25 cc. of 95% ethyl alcohol, let settle, decant off the supernatant liquid; boil residue with water, decant as before and boil residue with very dilute  $\text{NH}_4\text{OH}$ . If either the alcohol, water or  $\text{NH}_4\text{OH}$  is colored, organic coloring matter is indicated.

**Total Lead and Insoluble Residue.** Treat 1 gram with 15 cc. of  $\text{HNO}_3$  (1:1) and sufficient hydrogen dioxide to dissolve all the  $\text{PbO}_2$  on warming. If any insoluble matter is present, add 25 cc. of water, boil, filter and wash with hot water. Insoluble contains free  $\text{SiO}_2$ , and should be examined for  $\text{BaSO}_4$  and silicates, if appreciable. To the original solution or filtrate from insoluble, add 20 cc. of conc.  $\text{H}_2\text{SO}_4$  and evaporate to  $\text{SO}_3$  fumes; cool and determine lead as lead sulphate either gravimetrically or volumetrically. If the sample contains soluble barium salts, the  $\text{PbSO}_4$  will contain  $\text{BaSO}_4$  and should be treated with acid-ammonium acetate solution, the lead being determined in the filtrate.

**Determination of Lead Peroxide ( $\text{PbO}_2$ ) and True Red Lead ( $\text{Pb}_3\text{O}_4$ ).** (Method of Dichl,<sup>1</sup> modified by Topf<sup>2</sup>—not applicable when substances are present, other than oxides of lead, that liberate iodine under conditions given.)

Weigh 1 gram of finely ground sample into a 200-cc. Erlenmeyer flask, add a few drops of distilled water and rub the mixture to a smooth paste with a glass rod flattened on end. Mix in a small beaker 30 grams of C.P. "Tested Purity" crystallized sodium acetate, 2.4 grams of C.P. potassium iodide, 10 cc. of water and 10 cc. of 50% acetic acid; stir until all is liquid, warming gently; if necessary add 2 to 3 cc. of  $\text{H}_2\text{O}$ , cool to room temperature and pour into the flask containing the red lead. Rub with the glass rod until nearly all the red lead has been dissolved; add 30 cc. of water containing 5 or 6 grams of sodium acetate, and titrate at once with decinormal sodium thiosulphate, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow, rub any undissolved particles up with the rod until free iodine no longer forms, wash off rod, add the sodium thiosulphate solution until pale yellow, add starch solution and titrate until colorless, add decinormal iodine solution until blue color is just restored and subtract the amount used from the volume of thiosulphate that had been added.

**Calculation.** The iodine value of the sodium thiosulphate solution multiplied by 0.94193 =  $\text{PbO}_2$ ; the iodine value multiplied by 2.69973 =  $\text{Pb}_3\text{O}_4$ ; the  $\text{PbO}$  value multiplied by 2.86616 =  $\text{Pb}_3\text{O}_4$ .

**Sodium Thiosulphate Solution (decinormal).** Dissolve 24.83 grams of C.P. sodium thiosulphate, freshly pulverized and dried between filter paper, and dilute with water to 1 liter at a temperature at which the titrations are to be made. The solution should be made with well-boiled  $\text{H}_2\text{O}$ , free from  $\text{CO}_2$ , or let stand eight to fourteen days before standardizing. Standardize with pure, resublimed iodine, as described in the chapter on Iodine, page 204, and also against pure potassium iodate. The two methods of standardization should agree within 0.1% on iodine value.

**Starch Solution.** Two to 3 grams of potato starch are stirred up with 100 cc. of 1% salicylic acid solution, and the mixture boiled till the starch is practically dissolved and then diluted to 1 liter.

The red lead may also be examined for zinc, carbon dioxide, and soluble sulphate.

<sup>1</sup> Dingl. Polyt. Jour., 246, 196.

<sup>2</sup> Zeitschrift für analytische Chemie, 26, 206.

The second method for determination of the lead peroxide or true red lead content is somewhat shorter.<sup>1</sup>

Treat 1 gram in a beaker with 15 cc. of nitric acid, sp.gr. 1.2 (110 cc. nitric acid, sp.gr. 1.42 to 100 cc. of water). Stir the sample until all trace of red color has disappeared. Add from a calibrated pipette or burette exactly 10 cc. of dilute hydrogen dioxide (1 part of 3% hydrogen dioxide to 3.5 parts of water). Add about 50 cc. of hot water and stir until all the lead dioxide has passed into solution. In the case of some coarsely ground oxides the contents of the beaker may have to be gently heated to effect complete solution. After the oxide has completely passed into solution, dilute with hot water to about 250 cc. volume and titrate directly with a standard potassium permanganate solution, having an iron value of 0.005. Titrate to the faint pink permanganate color. A blank titration on the hydrogen dioxide solution must now be made.

Into a beaker pour 15 cc. of nitric acid of above strength and add exactly the same amount of hydrogen dioxide (10 cc.). Dilute to 250 cc. with hot water and titrate with standard potassium permanganate solution to a faint pink color.

The difference between the number of cc. of potassium permanganate required for the blank titration and the number required for the red lead titration is the amount required for the hydrogen dioxide which was reacted on by the red lead. The difference between the two amounts of potassium permanganate required multiplied by 3.058 grams gives the percentage of red lead present. The difference multiplied by 1.067 gives the percentage of  $PbO_2$  present.

### VERMILION

The following portion of Walker's<sup>2</sup> method, will suffice for the examination of this pigment. Should the analyst desire to determine the sulphide of mercury present or make a more complete examination—reference may be made to the original method.

True vermilion, or, as it is generally called, English vermilion, is sulphide of mercury. On account of its cost it is rarely used in paints, and is liable to gross adulteration. It should show no bleeding on boiling with alcohol and water and no free sulphur by extraction with carbon disulphide. A small quantity mixed with five or six times its weight of dry sodium carbonate and heated in a tube should show globules of mercury on the cooler portion of the tube. The best test for purity is the ash, which should be not more than one-half of 1%. Make the determination in a porcelain dish or crucible, using 2 grams of the sample. Ash in a muffle or in a hood with a very good draft, as the mercury fumes are very poisonous. It is seldom necessary to make a determination of the mercury.

Genuine vermilion is at the present time little used in paints. Organic lakes are used for most of the brilliant red, scarlet and vermilion shades. These organic coloring matters are sometimes precipitated on red lead, orange mineral or zinc oxide; but as a usual thing the base is barytes, whiting or china clay. Paranitriline red, a compound of diazotized paranitriline and beta-naphthol, is largely employed; but a number of colors may be used.

Paranitriline red is soluble in chloroform. It is also well to try the solvent

<sup>1</sup> "Analysis of Lead and Its Compounds," Schaeffer and White, pp. 25-27.

<sup>2</sup> P. H. Walker, Bulletin 109, Revised, Bureau of Chemistry, U. S. Dept. of Agri., pp. 31-33.

action on different reds, of sodium carbonate, etc. The amount of organic pigment present in such reds is generally very small, and when it cannot be determined by ignition owing to the presence of lead, zinc or carbonate, it is best determined by difference.

### IRON OXIDES

The iron oxides and manganese oxide pigments include the ochres, umbers, siennas, Venetian red, metallic brown, Indian red and Tuscan red.

In analyzing these pigments, the following constituents are sought; moisture, loss on ignition, insoluble residue, iron oxide, manganese dioxide, calcium and magnesium oxides and sulphur trioxide.

Owing to the similarity of the methods used for the analysis of these pigments to those used in the analysis of iron ores, the analyst is referred to p. 247 on the Analysis of Iron Ores, or to the method of Walker.<sup>1</sup>

### BLUE PIGMENTS

In examining blue pigments, only three are found of commercial importance in the manufacture of paints; namely, Prussian blue, ultramarine blue and sublimed blue lead.

Sublimed blue lead is the fume product resulting from the smelting of lead ores. In composition it consists of lead sulphate, lead sulphide, lead sulphite, lead oxide and zinc oxide, with occasional traces of carbon. It is finding its greatest use as an inhibitive pigment for the protection of iron and steel. Its color is a bluish gray.

Prussian blue is the double iron and potassium salt of hydroferrocyanic and hydroferricyanic acids.

Ultramarine blue is essentially a silicate and sulphide of sodium and aluminum.

### ULTRAMARINE BLUE

**Moisture.** Heat 2 grams at 105° C. for two hours.

**Silica.** Digest 1 gram with 30 cc. of concentrated HCl, taking care to avoid spattering. Evaporate to dryness, dehydrate, moisten with conc. HCl, dehydrate a second time, dilute, filter, and determine the silica by volatilization with H<sub>2</sub>SO<sub>4</sub> and HF.

**Aluminum Oxide.** In the filtrate from the silica, precipitate the aluminum hydroxide and determine in the usual manner. Report as aluminum oxide.

**Sodium Oxide.** The filtrate, after the removal of the aluminum hydroxide is acidified with H<sub>2</sub>SO<sub>4</sub>. Evaporate to dryness, ignite at a low red heat, and weigh the sodium sulphate. Calculate to sodium oxide.

**Total Sulphur.** Fuse 1 gram with a mixture of KNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>. Dissolve the fused mass in HCl, boil with conc. HNO<sub>3</sub> for one-half hour, remove the insoluble residue and determine the sulphuric acid in the usual way.

**Sulphur Present as Sulphate.** Dissolve 1 gram in dilute HCl and boil until all the hydrogen sulphide is removed. Filter off the insoluble residue and determine the sulphate in the filtrate.

<sup>1</sup> Bulletin 109, Revised, Bureau of Chemistry, U. S. Dept. Agri., pp. 33-34.



**PRUSSIAN BLUE—(CHINESE BLUE)—ANTWERP BLUE**

**Moisture.** Heat 2 grams at 105° C. for two hours. Dry Prussian blue should contain less than 7% moisture.

**Nitrogen.** Determine the nitrogen present by the Kjeldahl-Gunning method.

**Iron and Aluminum Oxides.** Ignite 1 gram at a low temperature, sufficient to decompose all the blue, but not to render the iron difficultly soluble. Digest the residue with (1 : 1) HCl. Any insoluble residue is examined for silica, barium sulphate and alumina. A pure Prussian blue should show no insoluble residue. The filtrate is examined for alumina, iron and calcium in the usual way.

An aliquot portion of the filtrate after the removal of the calcium is examined for the alkaline metals. Calculate any alkaline metal present to sulphate.

**Sulphuric Acid.** Determine the sulphuric acid in an aliquot portion after removal of the calcium.

**Commercial Analysis.** The method of Parry and Coste<sup>1</sup> is sufficiently accurate to determine the Prussian blue in most instances.

By multiplying the percentage of iron by 3.03 or the percentage of nitrogen by 4.4, the percentage of Prussian blue is directly determined.

In the case of Chinese blue, tin salts are frequently found. The presence of these salts should be sought by a qualitative examination.

**SUBLIMED BLUE LEAD<sup>2</sup>**

**Total Lead.** The total lead content is determined by the volumetric method for lead as outlined under Sublimed White Lead.

**Total Sulphur.** Treat 0.5 gram with 10 cc. of water and a few cc. of bromine water. Boil gently until all the bromine has passed off. Dilute with water, add another portion of bromine water, boil, and continue the treatment until the sediment has become white in color. Add 8 cc. of nitric acid, evaporate until the brown fumes of nitric acid have disappeared, dilute with water and add an excess of sodium carbonate. Determine as outlined under Zinc Lead and Leaded Zinc.

**Lead Sulphate.** On a separate sample determine the sulphate directly as outlined under Zinc Lead and Leaded Zinc, without any preliminary treatment for the oxidation of sulphites and sulphides.

**Lead Sulphite.** Boil 1½ grams with 3 grams of sodium carbonate. Allow to stand, filter and thoroughly wash. Treat the filtrate with bromine water as outlined under Total Sulphur and determine the combined sulphur present as sulphate and sulphite. Deduct the amount present as sulphate and calculate to sulphite.

**Lead Sulphide.** Deduct the sulphur present as sulphate and sulphite from the total sulphur and report the difference as lead sulphide.

**Lead Carbonate.** Determine any CO<sub>2</sub> present by the evolution method and calculate to lead carbonate. See p. 121, Vol. I.

**Lead Oxide.** Deduct the lead present as sulphate, sulphite, sulphide and carbonate from the total lead and report the difference as lead oxide.

<sup>1</sup> The Analyst, 21, 225-230, 1896.

<sup>2</sup> "The Chemical Analysis of Lead and its Compounds," Schaeffer and White, pp. 22-24.

**Zinc Oxide.** Determine the zinc volumetrically as outlined under Sublimed White Lead and report as zinc oxide.

**Carbon and Volatile Matter.** Ignite the sample in a partially covered crucible at a low heat for two hours. Report the difference in weight as carbon and volatile matter.

## YELLOW AND ORANGE PIGMENTS

### Chrome Yellows—American Vermilion—Basic Lead Chromate

The pigments under this class all contain chromates, with the exception of orange mineral, which is analyzed as under Red Lead. Frequently they contain lead sulphate and sometimes lead carbonate. A pure chrome yellow should contain only lead chromate and insoluble lead compounds. Owing to the frequent use of organic colors to brighten up the pigment, it is essential that a test be made for organic colors as outlined under Vermilion.

The analysis of these pigments is carried out in the following manner:

**Moisture.** Heat 2 grams at  $105^{\circ}$  C. for two hours.

**Insoluble Residue.** Treat 1 gram with 25 cc. of concentrated HCl, boil and during the boiling add a few drops of alcohol, one at a time. The solution is diluted to 100 cc., the boiling is continued for ten minutes and any insoluble residue is filtered off, thoroughly washed and examined for silica, barium sulphate and alumina.

**Lead.** The solution is nearly neutralized with  $\text{NH}_4\text{OH}$  and the lead is precipitated as  $\text{PbS}$  with  $\text{H}_2\text{S}$ . Filter off the precipitate of  $\text{PbS}$ , dissolve in  $\text{HNO}_3$ , add  $\text{H}_2\text{SO}_4$ , boil to strong fumes and determine as outlined under Sublimed White Lead or weigh as  $\text{PbSO}_4$ .

**Chromium.** The filtrate from the lead precipitation is boiled until all the  $\text{H}_2\text{S}$  is driven off. The solution is rendered alkaline with  $\text{NH}_4\text{OH}$  and the chromium is precipitated and determined as chromic oxide. Calculate to chromic anhydride.

**Zinc, Calcium and Magnesium.** Precipitate the zinc in the filtrate with  $\text{H}_2\text{S}$  and determine as previously outlined, either volumetrically or gravimetrically.

In the filtrate from the zinc precipitation, determine the calcium and magnesium in the usual manner.

If any carbonates are present, determine by the evolution method.

**Sulphuric Acid.** Determine the total sulphate as outlined under Zinc Lead and Leaded Zinc on p. 1183.

**Calculations.** Any chromic anhydride is calculated to lead chromate, sulphuric acid to lead sulphate, if calcium sulphate is absent, and any residual lead is calculated to lead oxide.

## GREEN PIGMENTS

### Chrome Green

Green pigments are usually mixtures of chrome yellow and Prussian blue, though organic color is sometimes present, which may be determined by an extraction with alcohol.

A microscopic examination should be made to determine whether the green is a combined precipitation product, which is of the greater value, or one mixed

after separate precipitation. A good green will show the presence of green and blue particles, while a poor green will show yellow and blue particles mixed with green. The analysis may be carried out as follows:<sup>1</sup>

**Moisture.** Heat 2 grams at 105° C. for two hours.

**Insoluble Residue.** Heat 1 gram at a low heat until the blue color has been decomposed, keeping the temperature sufficiently low so as not to render any of the iron or lead chromate insoluble. Determine the insoluble residue as outlined under Yellow Pigments, on p. 1195.

**Lead.** Determine as outlined under Yellow Pigments.

**Iron, Alumina and Chromium.** All the H<sub>2</sub>S is expelled from the filtrate after the lead precipitation by boiling. Add a few drops of HNO<sub>3</sub>, boil a few minutes and precipitate the aluminum, iron and chromium hydroxides with NH<sub>4</sub>OH. Filter, wash, dissolve the precipitate in HCl, and make up the solution to a definite volume.

In one portion the three hydroxides are precipitated together with NH<sub>4</sub>OH and weighed. Another portion is treated in a flask with an excess of KOH and bromine water until the iron hydroxide has assumed its characteristic reddish-brown color. Dilute with water, filter, wash and determine the iron in the usual way. Render the filtrate from the iron precipitation acid with HNO<sub>3</sub>, precipitate the aluminum hydroxide with NH<sub>4</sub>OH and weigh as Al<sub>2</sub>O<sub>3</sub>.

Chromium is determined in the filtrate by reduction to a chromic salt with HCl and alcohol, precipitated with NH<sub>4</sub>OH and weighed as oxide. Any method for the separation of the above hydroxides may be used in place of the one outlined.

**Calcium and Magnesium.** These constituents are determined in the filtrate from the precipitation of the above hydroxides.

**Sulphuric Acid.** One gram after ignition until all the blue has been decomposed, is dissolved in 30 cc. of conc. HCl, diluted with water, boiled, filtered, and washed. The sulphuric acid is determined in the filtrate.

**Nitrogen.** Determine as outlined under Prussian Blue.

**Calculation.** The Prussian blue is determined by multiplying the iron found by 3.03 or the nitrogen formed by 4.4. The sulphate is calculated to lead sulphate and calcium sulphate, should calcium be present, and the chromium to lead chromate.

## BLACK PIGMENTS

The black pigments include those which contain carbon as their essential constituent. The introduction of many black pigments which are made from asphaltic and coal-tar mixtures complicates their chemical analysis. For those pigments which contain coal-tar mixtures, recourse may be had to works<sup>2</sup> covering this matter thoroughly.

The analysis of the simple black pigments may be carried out in the following way:

**Moisture.** Dry 2 grams at 105° C. for two hours.

**Oil.** Extract 2 grams, with ether in a fat-extraction apparatus.

**Carbon.** Determine the carbon by difference after determining the moist-

<sup>1</sup> "The Analysis of Paints," Gardner and Schaeffer, pp. 36-37.

<sup>2</sup> Allen's "Commercial Organic Analysis," 4th Edition; "The Analysis of Paints," Gardner and Schaeffer.

ure, oil and ash. For an exact determination of carbon make a combustion test, absorbing the carbon dioxide in soda-lime or caustic potash as usual.

**Ash.** Ignite 2 grams to a bright red heat until all the carbon is driven off. If graphite is present, the ignition must be carried out with the aid of oxygen. Should carbonate be present, mix the ash with a small amount of ammonium carbonate and again ignite, thus reconverting to carbonate any oxide which may have been decomposed.

**Analysis of Ash.** The ash is boiled with concentrated HCl and the insoluble residue determined in the usual manner. The filtrate is examined for calcium, magnesium and phosphoric acid.

Calculate the magnesium to phosphate, any residual phosphoric acid to calcium phosphate and any residual calcium to carbonate.

### REFERENCES

The United States Interdepartmental Committee on Paint Specification Standardization, of which one of the writers is a member, has drawn up a series of specifications and methods of analysis for a wide series of painting materials. These specifications and methods have been published as circulars by the United States Bureau of Standards and may be secured for a nominal sum from the Superintendent of Public Documents, Government Printing Office, Washington, D. C.

The analyst is referred to the following circulars on this subject:

Basic Sulphate of Lead, Circular No. 85.

Basic Carbonate White Lead, Circular No. 84.

Leaded Zinc Oxide, Circular No. 88.

Zinc Oxide, Circular No. 87.

White Paint and Tinted Paints on a White Base, Circular No. 89.

Flat Interior Lithopone Paint, Circular No. 111.

Red Lead, Circular No. 90.

Ochre, Iron Oxide and Iron Hydroxide Paints, Circulars Nos. 91 and 93.

Green Paint, Circular No. 97.

Black Paint, Circular No. 94.

## COMPLEX COMPOUNDS—FERRO AND FERRI CYANIDES

### Hydroferrocyanic Acid

One gram of the hydroferrocyanide in 100 cc. of water acidified with 10 cc. of sulphuric acid is titrated in a casserole with standard potassium permanganate to a permanent pink color. The end-point is poor, so that it is advisable to standardize the permanganate against pure potassium ferrocyanide.

Reaction:  $2\text{H}_4\text{Fe}(\text{CN})_6 + \text{O} = \text{H}_2\text{O} + 2\text{H}_2\text{Fe}(\text{CN})_6$

One cc. N  $\text{KMnO}_4 = 0.3683$  gram  $\text{K}_4\text{Fe}(\text{CN})_6$ .

### Hydroferricyanic Acid

Ten grams of hydroferricyanide are dissolved in water, the solution made alkaline with KOH and heated to boiling and an excess of ferrous sulphate solution added. The yellowish brown ferric hydroxide turns black with excess of ferrous salt. The solution is diluted to exactly 500 cc. and 50 cc. of a filtered portion titrated with potassium permanganate.

One cc. N  $\text{KMnO}_4 = .3292$  gram  $\text{K}_3\text{Fe}(\text{CN})_6$ .

# CEMENT

RICHARD K. MEADE<sup>1</sup>

## ANALYSIS AND TESTING OF CEMENTS

The tests ordinarily applied to Portland cement are as follows:

Fineness.  
Specific gravity.  
Setting time.  
Soundness.  
Tensile strength.

Chemical analysis is also made, particular attention being paid to the determination of magnesia, sulphur trioxide, and loss on ignition. As a general rule, however, it may be said that so far as the consumer is concerned, more attention is paid to the physical tests than to chemical analysis.

Standard specifications covering the requirements for cement, both chemical and physical, have been adopted by the American Society for Testing Materials, and by the U. S. Government. The former are generally recognised by cement users as the standard requirements, while the latter are used by the various branches of the federal government.

The methods of making these tests follow.

## PHYSICAL TESTING

**Fineness.** The fineness of cement is usually determined by sieving a weighed portion through sieves having openings of definite sizes and observing the percentage of residue caught upon these. The standard sieves for cement testing are the No. 100 and the No. 200. The No. 100 cement test sieve has 100 openings to the linear inch and is called the 100-mesh sieve. Since the size of these openings will be influenced by the size of the wire used to weave the cloth of the sieve, the No. 100 sieve is made of wire having a diameter of 0.0045 in. As it is practically an impossibility to obtain wire having exactly 100 meshes to the linear inch, any sieve will be considered standard which contains from 96 to 100 meshes to the linear inch and is made of brass wire of the proper diameter (0.0045 inch). Similarly the No. 200 sieve (200-mesh) should contain between 192 and 208 meshes to the linear inch and be made of brass wire 0.0021 in. in diameter. The spacing should be regular, and in purchasing a new lot of sieves the number of meshes in each should be counted, and the cloth examined for irregularities. The sieves should be about 8 ins. in diameter, 2½ ins. deep and provided with a cover and a pan 2 ins. deep. The standard specifications

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and the U. S. Government specifications require the following degree of fineness:

*Cement.*

Residue on No. 200 sieve, not over..... 22%

There are now no longer any requirements as to fineness where listed with the No. 100 sieve.

The method of making the test is as follows: The cement to be tested is dried for one hour, in an air bath, at a temperature of from 100 to 110° C. (212 to 230° F.); 50 grams of this are then weighed into the No. 200 sieve, which should also contain a few large (B.B. size) buck-shot and have its pan attached. The cover is now placed on the sieve and the latter held in one hand, in a slightly inclined position, and moved forward and backward, at the same time striking the side gently with the palm of the other hand, at the rate of about 150 strokes per minute. The operation is continued until not more than one-tenth of 1% (0.05 gram) passes through after one minute of continuous sieving. The residue is then weighed, placed on the No. 100 sieve and the operation repeated. The results should be reported to the nearest tenth of 1%.

**Specific Gravity.** The standard instrument for determining specific gravity is the one designed by Le Chatelier, which is shown in Fig. 93. This consists of a flask of 120 cc. capacity, the neck of which is about 20 cm. long. In the middle of this neck is a bulb, above and below which are two marks. The volume between these marks is 20 cc., and the neck, which has a diameter of 9 mm., is graduated into tenths of cc. above the bulb.

In making the determination, which can be done in either of two ways, benzine (62° Bé. naphtha) or kerosene free from water should be used, and the sample of cement should be dried for at least one hour at from 100 to 110° C. and cooled to room temperature. To make the test fill the flask to the mark *E* with the liquid, next weigh out exactly 64 grams of cement and introduce into the neck of the flask by means of a funnel. The funnel stem should reach below the mark, *F*, on the stem, so that should any of the liquid fall against the side of the neck, it will be below the space eventually occupied by the liquid. The cement is added cautiously towards the last until the liquid fills the bulb, *C*, and rises to the mark, *F*, on the stem. The remainder of the cement is then weighed, and from this the weight of cement which displaces 20 cc. is calculated. From which

$$\text{Specific gravity} = \frac{\text{Difference}}{20}.$$

Instead of the above method the operator may add the entire 64 grams of cement. This will bring the surface of the liquid to one of the divisions on the

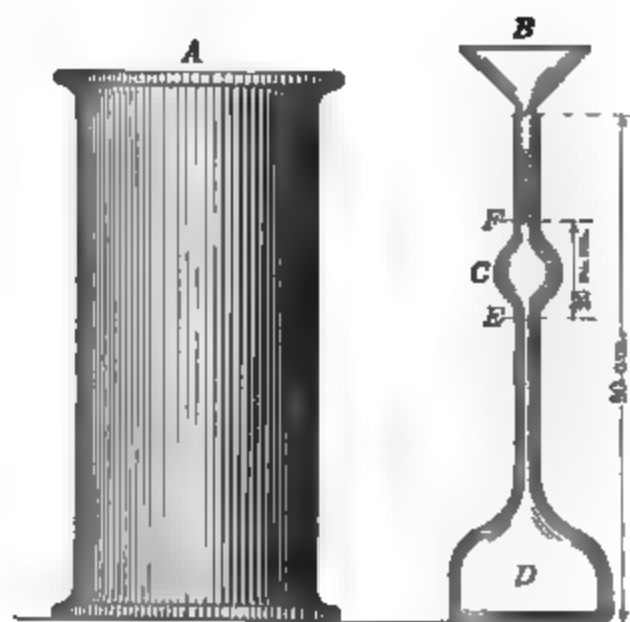


FIG. 93.

Le Chatelier's Specific Gravity Apparatus.

neck above the mark, *F*. This reading on the neck plus 20 will give the number of cc. displaced by 64 grams of cement. Then:

$$\text{Specific gravity} = \frac{64}{20 + \text{Reading on neck}}$$

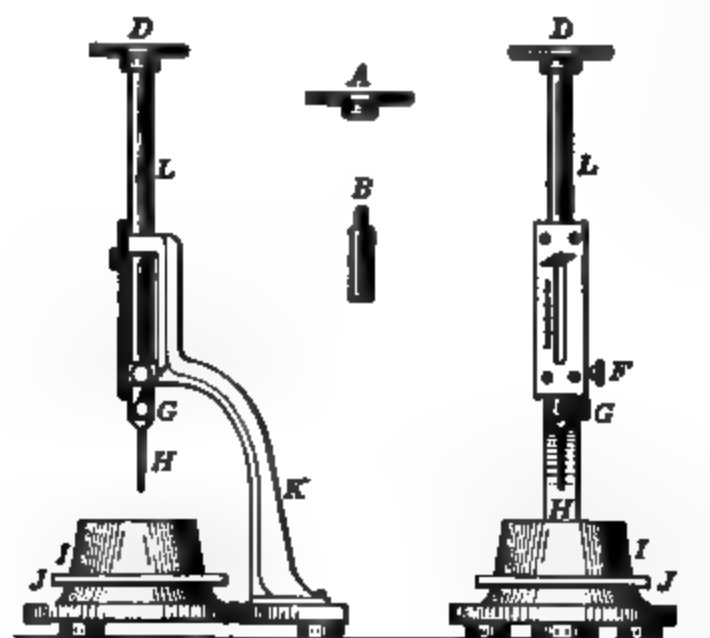
Care must be taken to keep the temperature of the liquid constant during the test.

The standard specifications require a specific gravity of at least 3.10.

**Normal Consistency.** In order to properly make the pastes and mortars used in the following tests, the amount of water to be used to make a paste or mortar of a definite state of plasticity, called "Normal Consistency," must be determined. The "standard specification" prescribes for doing this the Vicat needle. This consists of a frame, *K*, Fig. 94, bearing a movable rod, *L*, with the cup, *A*, at one end, and at the other, the cylinder, *B*, 1 cm. (0.39 in.) in

diameter, the cap, rod, and cylinder weighing 300 grams (10.58 oz.). The rod, which can be held in any desired position by a screw, *P*, carries an indicator, which moves over a scale (graduated to centimeters) attached to the frame, *K*. The paste is held by a conical, hard rubber ring, *I*, 7 cm. (2.76 ins.) in diameter at the base, 4 cm. (1.57 ins.) high, resting on a glass plate, *J*, about 10 cm. (3.894 ins.) square.

Five hundred grams of cement are placed on the mixing slab, which should be about 24 ins. square, and of plate glass or sheet brass. A crater is then formed in the center, into which the proper percentage of clean water is poured, and the material



VICAT NEEDLE.

FIG. 94.

turned into this crater by the aid of a trowel. As soon as the water has been absorbed, which should not require more than one minute, the operation is completed by a vigorous kneading with the hands, for one and a half minutes, the process being similar to that used in kneading dough. A sand-glass affords a convenient guide for the time of kneading. The hands should be protected by rubber gloves.

The paste is now formed into a ball, pressed into the rubber ring, through the larger opening, smoothed off and placed (on its large end) on a glass plate and the smaller end smoothed off with a trowel. The paste, confined in the ring, and resting on the glass plate, is placed under the rod having the cylinder, which is brought in contact with the surface and quickly released. The paste is of normal consistency when the cylinder penetrates to a point in the mass 10 mm. below the top of the ring. Great care should be taken to fill the ring exactly to the top.

Probably the majority of cement testers determine normal consistency by the ball test. This consists in forming the paste into a ball and dropping it

onto the table from a height of 18 ins. If of normal consistency the ball will neither flatten nor crack—the former if too wet and the latter if too dry. Most cements require about 20 to 24% of water for normal consistency.

The proper percentage of water for sand mortar is found from the following table, the first column of which gives the percentage of water found by trial as above to give normal consistency, and the second column shows the percentage of water for sand mortar.

PERCENTAGE OF WATER FOR STANDARD SAND MORTAR

Neat.	One cement, three standard Ottawa sand.	Neat.	One cement, three standard Ottawa sand.
15	9.0	21	10.3
16	9.2	24	10.5
17	9.3	25	10.7
18	9.5	26	10.8
19	9.7	27	11.0
20	9.8	28	11.2
21	10.0	29	11.3
22	10.2	30	11.5

**Setting Time.** In making the test, a paste of normal consistency is moulded and placed under the rod, *L*, Fig. 94, as described above; this rod, bearing the cap, *D*, at one end and needle, *H*, 1 mm. (0.039 in.) in diameter, at the other, weighing 300 grams (10.58 oz.). The needle is then carefully brought in contact with the surface of the paste and quickly released.

The cement has its *initial set* when the needle ceases to pass a point 5 mm. above the glass plate, in one-half minute after being released, and its *final set* the moment the needle ceases to sink visibly into the mass.

A simpler test, devised by Gen. Gilmore, is much more used than the above and consists of mixing cakes of neat cement, 3 ins. in diameter and  $\frac{1}{2}$  in. thick, to the consistency shown by the ball test and observing when they will bear a needle  $\frac{1}{8}$  in. in diameter weighted with  $\frac{1}{2}$  pound. This is noted at the initial set. The final set is the time after which they will bear a needle  $\frac{1}{8}$  in. in diameter weighted with 1 lb. In both cases the set is the time expressed in minutes between the mixing of the mortar and the failure of the needle to penetrate the surface.

The standard specifications call for a minimum initial set of 45 minutes, when the Vicat needle is used or sixty minutes where the Gilmore needle is used. The final set shall be attained within ten hours.

Fig. 95 shows the Gilmore needles. The pats should be made with a flat top (so as not to catch the edge of the needle as shown in Fig. 96) and if made to taper towards the edge may be used for the soundness test also. They should

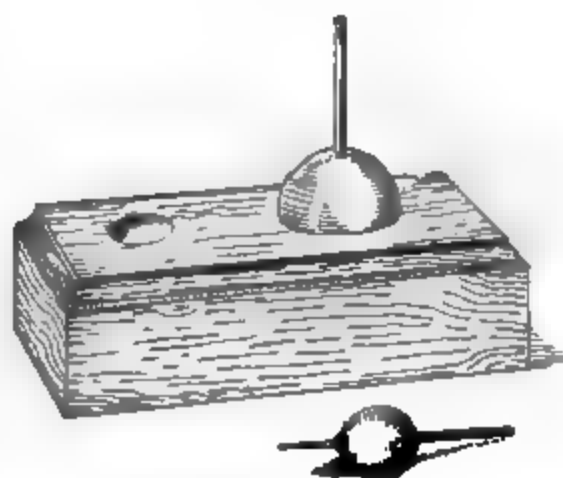


FIG. 95.—Gilmore Needles.



be kept in a moist closet or under a damp cloth to prevent drying out. A large covered tin box containing a wet sponge makes a good moist closet.



FIG. 96.—Pat for Determining Setting Time and Soundness.

**Soundness or Constancy of Volume.** For this test, which is intended to show the endurance of concrete made from the cement, pats about 3 ins. in diameter and  $\frac{1}{4}$  in. thick at the center, and tapering to a thin edge should be made upon a clean glass plate 4 ins. square. The paste from which the pats are made should be of normal consistency and they should be allowed to harden twenty-four hours in a moist closet. At the end of this time they should be exposed in an atmosphere of steam, 1 in. above boiling water, in a loosely covered vessel for three hours. At the end of this time the pats should show no signs of cracking, distortion, or disintegration. Distortion has not taken place if

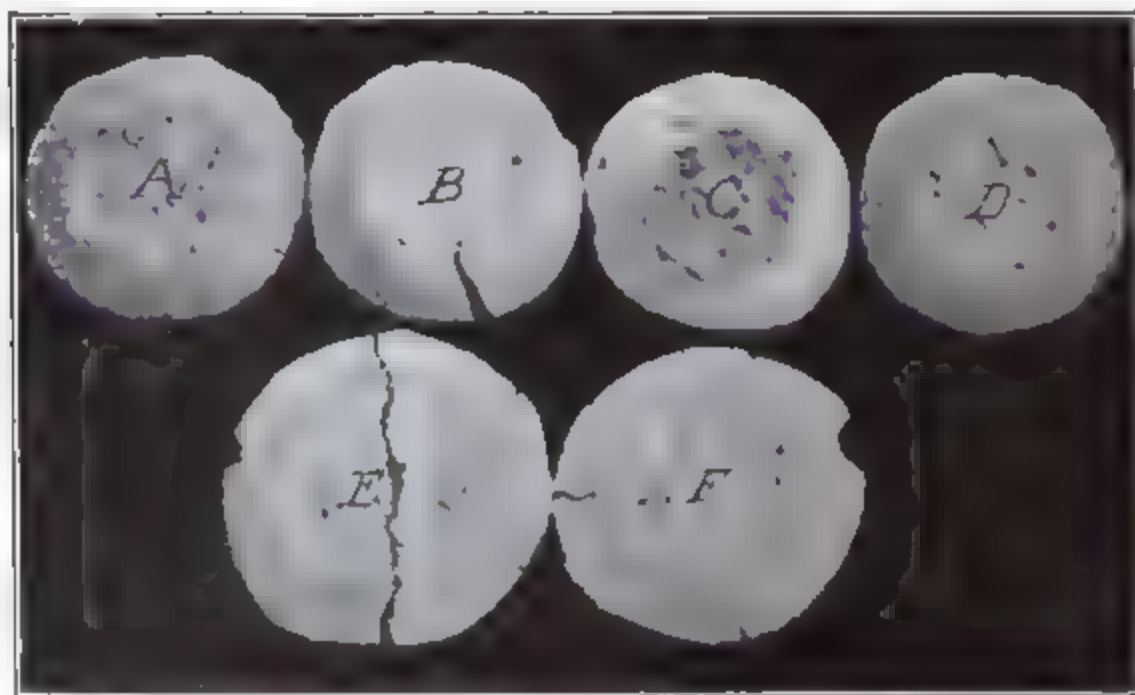


FIG. 97.—Appearance of Pats Made from Sound and Unsound Cement after Steaming

the pat sticks to the glass plate. Should it leave the plate, however, distortion may be detected by applying the edge of a ruler to the under side of the pat.

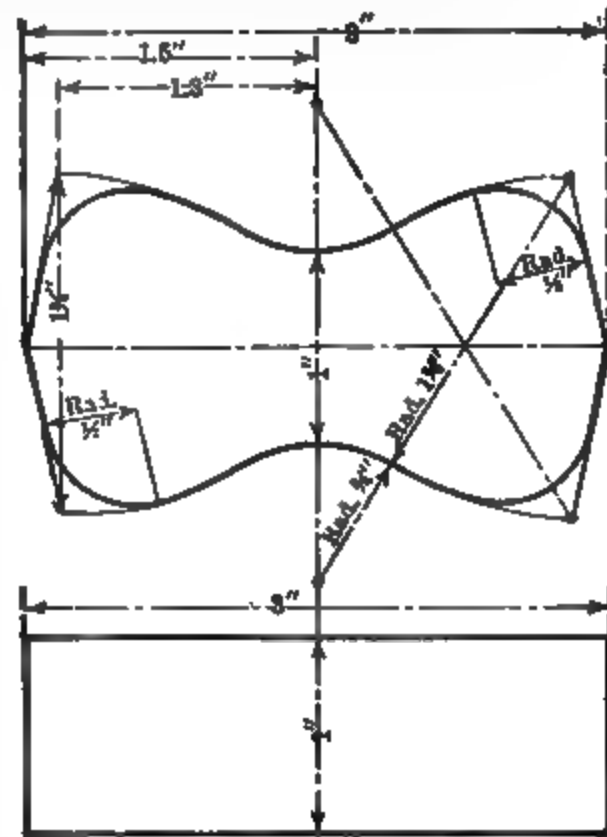
Fig. 97 shows six pats which have been steamed. Pats *E* and *F* have almost entirely disintegrated, while *B* is somewhat better and *A* and *D* almost sound. Pat *C* has stood the test successfully.

The cold-water test is also used (principally as a check upon the steam test) and consists in immersing a pat (similar to that used for steam) in cold water for twenty-eight days, at the end of which time it should show no signs of cracking, distortion, or disintegration.

The cracks due to disintegration should not be confused with those due to drying of the pat. The former are wedge shaped and radiate from the center of the pat, while the latter are usually running across the middle of the pat or around its edges. Shrinkage cracks due to drying are usually developed in a day or so, and are due to too thin (wet) a paste. Disintegration cracks rarely appear until after two or three days, and are due to expansives in the cement. The cracking of the glass to which the pat is attached during boiling means nothing to condemn the cement, and is due merely to unequal expansion of the pat and glass by the heat and a firm adhesion of the one to the other.

Where only a few tests have to be made, a convenient form of boiler consists of a tin bucket provided with a tin top. A few holes to permit exit of the steam are made in the top and a shelf of wire net or perforated tin is placed in the bucket. The pats are set on this and should be at least 2 ins. above the water.

**Tensile Strength.** The tensile strength of cement is tested both neat and with sand. In both tests the paste or mortar is moulded into a test-piece called a briquette, shown in Fig. 98, the least cross-section of which is 1 sq.in. in area. The moulds (Fig. 99) should be made of brass or bronze. They are made to permit of the making of but one briquette at a time (single moulds) or to permit of moulding a number of briquettes simultaneously (gang moulds):

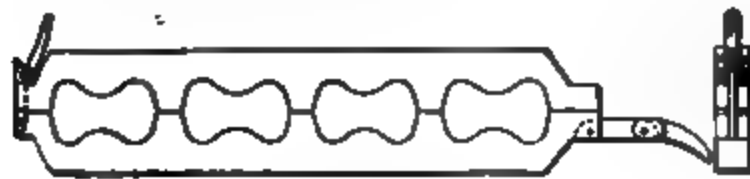


DETAILS FOR BRIQUETTE.

FIG. 98.

The mortar is mixed just as described under the heading "Normal Consistency," about 125 grams of cement being used for each neat briquette, or 500 grams for a gang of four briquettes.

Immediately after mixing the mortar or paste, the moulds should be filled, the material pressed in firmly with the fingers and smoothed off with a trowel



DETAILS FOR GANG MOULD.

FIG. 99.

without ramming; the material should be heaped up on the upper surface of the mould, and, in smoothing off, the trowel should be drawn over the mould in such a manner as to exert a moderate pressure on the excess

materials. The mould should be turned over and the operation repeated.

The moulds containing the briquettes should then be kept in a moist closet, or under a damp cloth until the briquettes have hardened sufficiently to remove from the moulds, usually in about four to eight hours. On removal from the mould, the briquettes should be kept in the moist closet until they are twenty-four hours old, when, with the exception of the one-day briquettes, which are broken immediately, they should be placed in water, kept at as near 21° C. as possible.

The briquettes are then removed from the water at intervals and *immediately* broken by means of some form of testing machine. Fig. 100 shows the Fairbanks cement-testing machine. In this machine the briquette is held in the clips, *N* and *N*, and a stress is applied to it through the levers, *C* and *R*, by the weight of fine shot falling into the bucket, *F*. After the specimen breaks the stress required to rupture it is found by weighing the shot; the beam, *R*, being graduated for this purpose. In placing the briquette in the clips great care

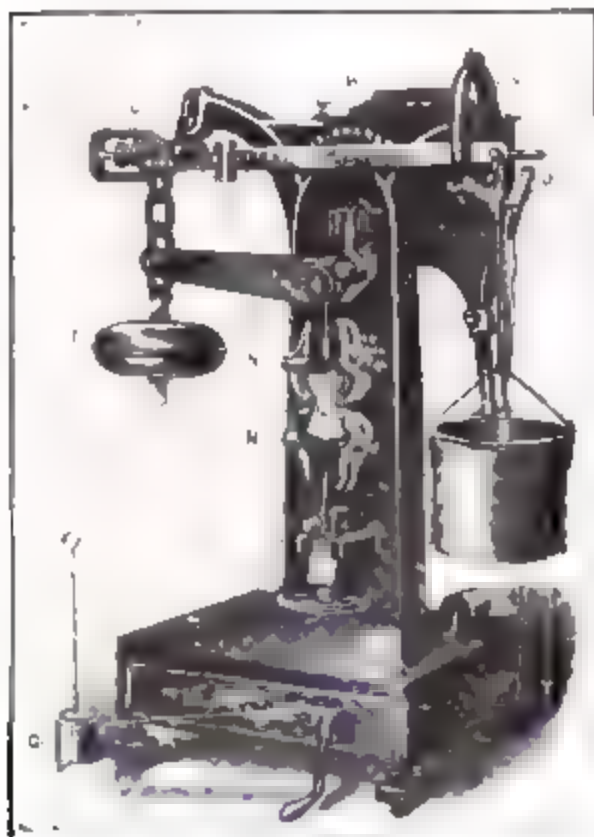


FIG. 100.  
Fairbanks Cement-testing Machine.

must be exercised to center it properly, as cross strains tend to lower the breaking strength. The briquettes must be broken as soon as they are removed from the water and the flow of shot into the bucket should be so regulated as to represent a load of about 600 lbs. per minute.

Fig. 101 shows the Riehle automatic cement-testing machine. This is a new type of machine which is coming into general use for cement testing, as it does away with some of the errors in the older form. In this type, the initial load is avoided by balancing a bucket of shot against a weight and the load is applied to the test specimen by allowing the shot to run out of the bucket. The load acting through the levers breaks the briquette when the shot is cut off by means of an automatic valve. The shot flowing out of the bucket are caught in a large cup resting on a spring scale which registers the load. This can be read as soon as the briquette breaks. The beam should be kept horizontal by means of the

lever and worm gear as shown by the pointer on the beam.

Briquettes are usually broken in series from two to five each. The periods of breaking are after one day, seven days, twenty-eight days, three months, six months, one year, two years, three years, five years, ten years, etc. The tests of one year and upwards are usually called long-time tests. In some laboratories only one-day, seven-day and twenty-eight-day tests are made. The one-day briquettes are broken exactly twenty-four hours after they are made, the seven-day briquettes seven days after, etc.

Sand briquettes are made of a mixture of one part cement and three of standard sand, and these are first mixed dry and then the water is added and the moulding done as for neat briquettes. The standard sand at the present time is a natural sand from Ottawa, Ill., which is obtained from the Ottawa Silica Sand Co., Sandusky, O. It should be screened to pass a sieve made of wires 0.0165 in. in diameter and of 20 meshes to the linear inch and to be retained by a 30-mesh sieve (of 0.0112 in. diameter wire). Some testers, however, use crushed quartz, such as is used in the manufacture of sand-paper, sized to pass a No. 20 sieve and be retained on a No. 30. The Ottawa sand, however, gives the higher results. No sand briquettes are usually broken for twenty-four hour periods.

The standard specifications require a minimum strength of 200 lbs. with sand after seven days, and 300 with sand after twenty-eight days, and also that the average figures in each case must be higher for the latter than for the former period.

The standard specifications now do not require a neat test to be made, but it is usually done for information.

**Notes.** After use, the moulds should be scraped free of hardened cement with a piece of soft metal (such as copper or zinc), brushed off with a stiff blacking brush, and wiped with a cloth and a little machine oil.

Neat briquettes should be marked with a stencil so as to identify them, and the sand briquettes placed in the water below the neat ones in such a manner as to identify the former. Usually the sand briquettes are placed edgewise in the water, and the corresponding neats are placed edgewise on top of the sand.

Small troughs or tanks consisting merely of galvanized iron pans, 3 ins. deep, may be purchased and will answer where only a few tests are to be made. Otherwise shallow wooden troughs lined with zinc will be found convenient. They may be placed one above the other.



FIG. 101.  
Riehle Automatic Cement-Testing Machine.

**Apparatus Needed for Cement Testing.** The following apparatus will be needed for cement testing:

1. Apparatus for specific gravity, Le Chatelier's.
2. Scale for fineness.
3. Sieve—100 mesh, standard.
4. Sieve—200 mesh, standard.
5. Vicat apparatus (or Gilmore needles).
6. Trowel—8 ins.
7. Rubber gloves.
8. Measuring glass—500 cc. capacity.
9. Slab of glass (or brass), 24×24 ins.
10. Scale, capacity, 1000 grams.
11. Weights for above scale.
12. Glass plates—4×4 ins.
13. Moulds.
14. Testing machine.
15. Standard sand.
16. Galvanized iron pan, 24×24×13 ins.

## STANDARD METHOD FOR CHEMICAL ANALYSIS OF PORTLAND CEMENT<sup>1</sup>

### Solution

One-half gram of the finely powdered substance is to be weighed out and, if a limestone or unburned mixture, strongly ignited in a covered platinum crucible over a strong blast for fifteen minutes, or longer if the blast is not powerful enough to effect complete conversion to a cement in this time. It is then transferred to an evaporating dish, preferably of platinum for the sake of celerity in evaporation, moistened with enough water to prevent lumping, and 5 to 10 cc. of strong HCl added and digested with the aid of gentle heat and agitation until solution is complete. Solution may be aided by light pressure with the flattened end of a glass rod.<sup>2</sup> The solution is then evaporated to dryness, as far as this may be possible on the bath.

### Silica ( $\text{SiO}_2$ )

The residue without further heating is treated at first with 5 to 10 cc. of strong HCl, which is then diluted to half strength or less, or upon the residue may be poured at once a larger volume of acid of half strength. The dish is then covered and digestion allowed to go on for ten minutes on the bath, after which the solution is filtered and the separated silica washed thoroughly with water. The filtrate is again evaporated to dryness, the residue, without further heating, taken up with acid and water and the small amount of silica it contains separated on another filter paper. The papers containing the residue are transferred wet to a weighed platinum crucible, dried, ignited, first over a Bunsen burner until the carbon of the filter is completely consumed, and finally over the blast for fifteen minutes and checked by a further blasting for ten minutes or to constant weight. The silica, if great accuracy is desired, is treated in the crucible with about 10 cc. of HF and 4 drops of  $\text{H}_2\text{SO}_4$ , and evaporated over a low flame to complete dryness. The small residue is finally blasted, for a minute or two cooled and weighed. The difference between this weight and the weight previously obtained gives the amount of silica.<sup>3</sup>

### Alumina and Iron ( $\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ )

The filtrate, about 250 cc., from the second evaporation for  $\text{SiO}_2$ , is made alkaline with  $\text{NH}_4\text{OH}$  after adding HCl, if need be, to insure a total of 10 to 15 cc. of strong acid, and boiled to expel excess of  $\text{NH}_3$ , or until there is but a faint odor of it, and the precipitated iron and aluminum hydrates, after settling, are washed once by decantation and slightly on the filter. Setting aside the filtrate, the precipitate is dissolved in hot dilute HCl, the solution passing into the

<sup>1</sup> Method Suggested for the Analysis of Limestones, Raw Mixtures, and Portland Cements by the Committee on Uniformity in Technical Analysis with the Advice of W. F. Hillebrand.

<sup>2</sup> If anything remains undecomposed it should be separated, fused with a little  $\text{Na}_2\text{CO}_3$ , dissolved and added to the original solution. Of course a small amount of separated non-gelatinous silica is not to be mistaken for undecomposed matter.

<sup>3</sup> For ordinary control in the plant laboratory this correction may, perhaps, be neglected; the double evaporation, never.



beaker in which the precipitation was made. The aluminum and iron are then reprecipitated by  $\text{NH}_4\text{OH}$ , boiled and the second precipitate collected and washed on the same filter used in the first instance. The filter paper, with the precipitate, is then placed in a weighed platinum crucible, the paper burned off and the precipitate ignited and finally blasted five minutes, with care to prevent reduction, cooled and weighed as  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ .<sup>1</sup>

### Iron ( $\text{Fe}_2\text{O}_3$ )

The combined iron and aluminum oxides are fused in a platinum crucible at a very low temperature with about 3 to 4 grams of  $\text{KHSO}_4$ , or, better,  $\text{NaHSO}_4$ , the melt taken up with so much dilute  $\text{H}_2\text{SO}_4$  that there shall be no less than 5 grams absolute acid and enough water to effect solution on heating. The solution is then evaporated and eventually heated till acid fumes come off copiously. After cooling and redissolving in water, the small amount of silica is filtered out, weighed and corrected by  $\text{HFl}$  and  $\text{H}_2\text{SO}_4$ .<sup>2</sup> The filtrate is reduced by zinc, or preferably by hydrogen sulphide, boiling out the excess of the latter afterwards while passing  $\text{CO}_2$  through the flask, and titrated with permanganate.<sup>3</sup> The strength of the permanganate solution should not be greater than .0040 gram  $\text{Fe}_2\text{O}_3$  per cc.

### Lime ( $\text{CaO}$ )

To the combined filtrate from the  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  precipitate a few drops of  $\text{NH}_4\text{OH}$  are added, and the solution brought to boiling. To the boiling solution 20 cc. of a saturated solution of ammonium oxalate are added, and the boiling continued until the precipitated  $\text{CaC}_2\text{O}_4$  assumes a well-defined granular form. It is then allowed to stand for twenty minutes, or until the precipitate has settled, and then filtered and washed. The precipitate and filter are placed wet in a platinum crucible, and the paper burned off over a small flame of a Bunsen burner. It is then ignited, redissolved in  $\text{HCl}$ , and the solution made up to 100 cc. with water. Ammonia is added in slight excess, and the liquid is boiled. If a small amount of  $\text{Al}_2\text{O}_3$  separates, this is filtered out, weighed, and the amount added to that found in the first determination, when greater accuracy is desired. The lime is then reprecipitated by ammonium oxalate, allowed to stand until settled, filtered, and washed,<sup>4</sup> weighed as oxide by ignition and blasting in a covered crucible to constant weight, or determined with dilute standard permanganate.<sup>5</sup>

### Magnesia ( $\text{MgO}$ )

The combined filtrates from the calcium precipitates are acidified with  $\text{HCl}$  and concentrated on the steam bath to about 150 cc., 10 cc. of saturated solution

<sup>1</sup> This precipitate contains  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Mn}_2\text{O}_3$ .

<sup>2</sup> This correction of  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  for silica should not be made when the  $\text{HFl}$  correction of the main silica has been omitted, unless that silica was obtained by only one evaporation and filtration. After two evaporations and filtrations 1 to 2 milligrams of  $\text{SiO}_2$  are still to be found with the  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ .

<sup>3</sup> In this way only is the influence of titanium to be avoided and a correct result obtained for iron.

<sup>4</sup> The volume of wash-water should not be too large; *vide* W. F. Hildebrand.

<sup>5</sup> The accuracy of this method admits of criticism, but its convenience and rapidity demand its insertion.

of  $\text{Na}(\text{NH}_4)\text{HPO}_4$  are added, and the solution boiled for several minutes. It is then removed from the flame and cooled by placing the beaker in ice water. After cooling,  $\text{NH}_4\text{OH}$  is added drop by drop with constant stirring until the crystalline ammonium-magnesium ortho-phosphate begins to form, and then in moderate excess, the stirring being continued for several minutes. It is then set aside for several hours in a cool atmosphere and filtered. The precipitate is redissolved in hot dilute  $\text{HCl}$ , the solution made up to 100 cc., 1 cc. of a saturated solution of  $\text{Na}(\text{NH}_4)\text{HPO}_4$  added, and ammonia drop by drop, with constant stirring until the precipitate is again formed as described and the ammonia is in moderate excess. It is then allowed to stand for about two hours, when it is filtered on a paper or a Gooch crucible, ignited, cooled and weighed as  $\text{Mg}_2\text{P}_2\text{O}_7$ . Portland cement must not contain more than 4% magnesia.

### Alkalies ( $\text{K}_2\text{O}$ and $\text{Na}_2\text{O}$ )

For the determination of the alkalies, the well-known method of Prof. J. Lawrence Smith is to be followed, either with or without the addition of  $\text{CaCO}_3$  with  $\text{NH}_4\text{Cl}$ .

### Anhydrous Sulphuric Acid ( $\text{SO}_3$ )

One gram of the substance is dissolved in 15 cc. of  $\text{HCl}$ , filtered and residue washed thoroughly.<sup>1</sup>

The solution is made up to 250 cc. in a beaker and boiled. To the boiling solution 10 cc. of a saturated solution of  $\text{BaCl}_2$  are added slowly drop by drop from a pipette and the boiling continued until the precipitate is well formed, or digestion on the steam bath may be substituted for the boiling. It is then set aside over night, or for a few hours, filtered, ignited and weighed as  $\text{BaSO}_4$ . Both specifications require cement to contain not more than 1.75%  $\text{SO}_3$ .

### Total Sulphur

One gram of the material is weighed out in a large platinum crucible and fused with  $\text{Na}_2\text{CO}_3$  and a little  $\text{KNO}_3$ , being careful to avoid contamination from sulphur in the gases from source of heat. This may be done by fitting the crucible in a hole in an asbestos board. The melt is treated in the crucible with boiling water and the liquid poured into a tall, narrow beaker and more hot water added until the mass is disintegrated. The solution is then filtered. The filtrate contained in a No. 4 beaker is to be acidulated with  $\text{HCl}$  and made up to 250 cc. with distilled water, boiled, the sulphur precipitated as  $\text{BaSO}_4$  and allowed to stand over night or for a few hours.

### Loss on Ignition

Half a gram of cement is to be weighed out in a platinum crucible, placed in a hole in an asbestos board so that about three-fifths of the crucible projects below, and blasted fifteen minutes, preferably with an inclined flame. The loss by weight, which is checked by a second blasting of five minutes, is the loss on ignition. This must not be more than 4%.

<sup>1</sup> Evaporation to dryness is unnecessary, unless gelatinous silica should have separated, and should never be performed on a bath heated by gas; *vide* W. F. Hildebrand.

May, 1903: Recent investigations have shown that large errors in results are often due to the use of impure distilled water and reagents. The analyst should, therefore, test his distilled water by evaporation and his reagents by appropriate tests before proceeding with his work.

### Insoluble Residue

In addition to the above the U. S. Government specifications require the cement to show not more than 1% insoluble residue as determined below.

A 1-gram sample is digested on the steam bath in HCl of approximately 1.035 sp.gr. until the cement is dissolved. The residue is filtered, washed with hot water, and the filter paper and contents digested on the steam bath in a 5% solution of sodium carbonate. The residue is then filtered, washed with hot water, then with hot HCl (1.035 sp.gr.) and finally with hot water, then ignited at a red heat and weighed. The quantity so obtained is the insoluble residue.

### RAPID METHOD FOR CHEMICAL ANALYSIS OF PORTLAND CEMENT<sup>1</sup>

Before submitting the cement to a chemical analysis it should be passed through a No. 100 test sieve to free it from pieces of clinker too large to be quickly attacked by the acid.

Weigh 0.5 gram of cement into a wide platinum or porcelain dish. The former is the more expensive of the two, but it is a better conductor of heat and there is no danger of contaminating the solution with silica, etc., from the dish, if the evaporation is conducted in platinum. The silica can also be entirely removed from a platinum dish. Now stir up the sample of cement in the dish with 10 cc. of cold water until all lumps are broken up, and add immediately 10 cc. of cold dilute hydrochloric acid (1 : 1). Place the dish on a water bath and evaporate to dryness, stirring occasionally. The water bath will evaporate as fast as anything else and there is no danger of the silica's spattering, which it is apt to do, unless the operation is very carefully watched, when a hot plate is used. As soon as the contents of the dish are dry, cool, add 10 cc. of dilute hydrochloric acid and 30 cc. of water, digest five or ten minutes on the hot plate, filter and wash ten times with hot water. Evaporate the filtrate to dryness. Cool, add 10 cc. of dilute hydrochloric acid and 50 cc. of water to the contents of the dish, cover with a watch-glass and digest on the hot plate for five or ten minutes. Filter off the slight residue of silica on a 9-cm. filter, wash well (seven to ten times) with hot water and put in a weighed platinum crucible together with the silica obtained from the first filtration. Ignite over the Bunsen burner until all the filter paper is consumed and then ignite strongly over a blast lamp for ten minutes. Cool in a desiccator and weigh as  $\text{SiO}_2$ ; multiply the weight by 200 for per cent of silica,  $\text{SiO}_2$ .

Heat the filtrate to boiling and add a faint but distinct excess of ammonia. This can be most conveniently done by means of a bottle, fitted with a siphon tube, the end of which terminates in a jet, connected to it by a short piece of rubber tubing, which is closed by a pinch cock. The bottle stands on a shelf

<sup>1</sup> Method used in the laboratories of most cement companies and for routine work.



over the reagent table, and the siphon extends to within six inches of the surface of the table. The beaker is placed under the jet, and the ammonia can be very carefully and conveniently added by pressing the pinchcock. After adding the ammonia replace the beaker on the hot plate and boil for five minutes. Remove from the hot plate and allow the precipitate to settle. Filter onto an 11-cm. filter paper and wash once with hot water to collect the precipitate in the cone of the filter. Invert the funnel over the beaker in which the precipitation was made and wash practically all of the precipitate into this, allowing the filter to remain in the funnel. Dissolve the precipitate in 20 cc. of 10% nitric acid (1 : 10) and dilute the solution to 100 cc. Heat to boiling and reprecipitate with ammonia as before. Boil for five minutes, allow the precipitate to settle and filter through the same filter paper as used for the first precipitation. Wash once with hot water. Ignite carefully in a weighed crucible over a Bunsen burner and finally blast for five minutes. Cool and weigh as combined oxides of iron and alumina,  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ . This precipitate also contains manganese dioxide, phosphoric and titanitic acids, all of which are present in small quantities in the cement. Determine the iron oxide as directed further on, and deduct from the combined weights for the alumina,  $\text{Al}_2\text{O}_3$  (phosphoric acid, titanitic acid, etc.).

Make the filtrate from the iron and alumina alkaline with ammonia; boil and add 20 cc. of boiling saturated ammonium oxalate solution (or better, 3 grams of solid ammonium oxalate dissolved in 25-50 cc. of boiling water just prior to use). Stir well, allow fifteen minutes to settle, filter on an 11-cm. filter, and wash ten times with hot water, using as little as possible (about 100-125 cc.) to do the work well. Proceed as in A or B.

A. Gravimetric. Place the precipitate in a weighed platinum crucible, ignite, and weigh, after ignition over a blast-lamp to constant weight, as calcium oxide,  $\text{CaO}$ . Report as such.

B. Volumetric. Transfer the paper and precipitate to the beaker in which the latter was formed, and opening, spread it out against the upper side of the beaker. Wash the precipitate off the paper with a jet of hot water, fold the paper over, add 50 cc. of dilute (10%) sulphuric acid (1 : 10) to the contents of the beaker, dilute to 150 cc. and heat until the liquid is between 60 and 90°

C. Titrate with permanganate solution until the pink color is produced. All this time the paper should be sticking to the walls of the beaker. Now drop this into the solution and stir. The pink color of the latter will be discharged. Finish the titration very carefully by adding permanganate, a drop at a time, and calculate the lime.

If the filtrate from the lime measures over 250 cc., acidify and evaporate until this bulk is reached. This can be rapidly done by using a large (8 in.) porcelain dish in the following manner: Place a piece of wire gauze on a tripod and in the center of this a round piece of thin asbestos paper about the size of a silver dollar. Now place the dish on this and a Bunsen burner turned fairly low under the asbestos dish. The contents of the dish can then be made to evaporate rapidly, without boiling, by regulating the flame. When the solution measures 250 cc., transfer to a beaker. If necessary, cool and, when perfectly cold, add 15 cc. of a 10% solution of sodium phosphate and 25 cc. of strong ammonia. Stir thoroughly and set aside in a cool place for at least six hours. Filter, wash with a mixture of water 800 cc., ammonia (0.96 sp.gr.) 200 cc., and ammonium nitrate 100 grams; place in a weighed platinum or porcelain crucible

and ignite over a low flame until all carbon is burned off. (Do not use the blast lamp.) Cool in a desiccator and weigh as magnesium pyrophosphate, which weight multiplied by 72.38 gives the percentage of magnesia,  $\text{MgO}$ .

Weigh 1 gram of finely ground cement into a small beaker and add 15 cc. of dilute hydrochloric acid, heat from ten to fifteen minutes and add a little water. Heat to boiling and filter<sup>1</sup> through a small filter, washing the residue well with water and catching the filtrate and washings in a small beaker. Add to the solution 5 cc. of dilute hydrochloric acid and bring to a boil. Add carefully, drop by drop, stannous chloride solution (25 grams in 100 cc. of dilute 1:3 hydrochloric acid) until the last drop makes the solution colorless. Add 3 drops in excess. Remove from the burner and cool the liquid by setting in a vessel of cold water. When nearly cold, add 15 cc. of saturated mercuric chloride solution and stir the liquid with a glass rod. Allow the mixture to stand for a few minutes, during which time a slight white precipitate should form. Run in standard bichromate solution carefully from a burette until a drop of iron solution tested with a drop of 1% solution of potassium ferricyanide no longer shows a blue, but instead a yellow color. Multiply the number of cc. of bichromate used by the ferric oxide equivalent per cc. of the bichromate and divide the product by the weight of the sample. The result multiplied by 100 gives the per cent of the ferric oxide in the cement. The most convenient strength for the standard bichromate solution is 3.074 grams of the salt to the liter. One cc. of this solution is equivalent to 0.005 gram ferric oxide. It should be standardized against iron wire or ferrous ammonium sulphate.

Weigh 1 gram of the sample into a small dry beaker and stir it up with 10 cc. of cold water until all lumps are broken up and the lighter particles are in suspension. Add 7.5 cc. of dilute (1:1) hydrochloric acid and heat until solution is complete. Filter through a small paper and wash the residue thoroughly. Dilute the filtrate to 250 cc., heat to boiling, and add 10 cc. of boiling 10% barium chloride solution. Stir well and allow to stand overnight. Filter, ignite, and weigh as  $\text{BaSO}_4$ , which, multiplied by 34.29, gives the percentage of  $\text{SO}_3$ .

Place one-half gram of the cement in a clean platinum crucible which has been previously ignited to redness and cooled in a desiccator. Cover with the lid and weigh. Ignite for fifteen minutes over a good blast lamp. Rinse off the crucible lid with hot water to remove volatile salts condensed on the latter. Ignite the lid to redness and cool the crucible and lid in a desiccator. Weigh and the loss in weight multiplied by 200 is "loss on ignition."

For the alkalies in cement see analysis of clay.

<sup>1</sup> May be omitted if the cement practically all dissolves. Most cements do.

## **RAPID METHOD FOR CHECKING THE PERCENTAGE OF CALCIUM CARBONATE IN CEMENT MIXTURE**

The following rapid method is generally used in the cement industry for checking the composition of the ground mixture of raw materials before these are fed into the kiln.

### **Standard Alkali**

This should be exactly  $2/5$  normal and may be prepared in any convenient manner. Usually 8 or 10 liters are made up at one time and kept in a bottle provided with a siphon tube and with a layer of coal oil on top of the solution about  $\frac{1}{2}$  in. thick to prevent the absorption of carbon dioxide by the caustic soda.

Phenolphthalein should be used as an indicator. A 1% solution of this is employed.

One cc. of  $2/5$  N alkali is equivalent to exactly 0.02 gram of  $\text{CaCO}_3$ , or to 2% where 1-gram sample is used.

### **Standard Acid**

Take the specific gravity of a bottle of hydrochloric acid, using a hydrometer for the purpose. Refer to a table of specific gravities of hydrochloric acid and calculate from this the quantity of acid necessary to contain 97.0 grams of HCl.

Measure this quantity of the acid into a liter flask and dilute to the mark, pour into an 8-liter bottle and add 7 liters of water, measuring with the flask. Mix the contents of the bottle well by shaking. Ten cc. of this solution should be equivalent to from 8.1 to 8.5 cc. of the  $2/5$  N alkali when checked by adding a drop of phenolphthalein solution and running in the alkali to a purple red color. If its value does not lie between these figures add acid or water to make it of this strength.

### **Standard Sample**

A standard sample of raw material is necessary to standardize the acid and alkali for actual use. This sample should be ground in the same manner as the daily run of samples to be checked by the acid and alkali. It should all pass a 100-mesh sieve and be freed from hygroscopic moisture, by drying for some hours, at  $110^\circ \text{C}$ . Three or four pounds of this sample should be prepared and kept in air-tight jars or bottles. A small sample (1 or 2 oz.) of this should be placed in a 2-oz. bottle and stoppered with a rubber cork when not in use. This small sample can then be redried for an hour at  $100\text{--}110^\circ \text{C}$ . and used for standardizing, avoiding the frequent opening and mixing of the contents of the large jars or bottles.

After drying, the standard sample should be carefully analyzed. It should contain approximately the quantity of carbonate of lime which it is desired to have in the mix, and the amount of magnesia should also be normal. When the magnesia varies at different times, fresh standard samples should be prepared to contain these varying percentages of magnesia; otherwise the lime will be reported incorrectly.

### Standardizing the Acid

Weigh 1 gram of the standard sample into a 600-cc. Erlenmeyer flask and run in from a pipette 50 cc. of standard acid. Close the flask with a rubber stopper, having inserted through it a long glass tube 30 ins. long and about  $\frac{1}{2}$  in. internal diameter. Heat the flask on a wire gauze over a burner as shown in Fig. 102 until steam *just begins* to escape from the upper end of the tube. The heating should be so regulated that the operation requires very nearly two minutes, from the time the heat applied, until steam issues from the tube. Remove the flask from the heat, as soon as the steam escapes from the tube, and rinse the tube into the flask, in the following manner. Rest the flask, still stoppered, on the table and grasp the tube between the thumb and forefinger of the left hand. Direct a stream of cold water, from a wash-bottle in the right hand, down the tube, holding the latter inclined at an angle of  $45^\circ$ , and rolling the flask from side to side on the table, in sweeps of 2 or 3 ft., by twirling the tube between the finger and thumb. Unstopper the flask and rinse off the sides and bottom of the stopper, into the flask, and wash down the sides of the latter. Add a drop or two of phenolphthalein and run in the standard alkali, from a burette, until the color changes to purple red. This color is often obscured until the organic matter settles, so it is necessary to hold the flask to the light and observe the change by glancing across the surface. A little practice will easily enable the operator to carry on the titration with accuracy and precision.

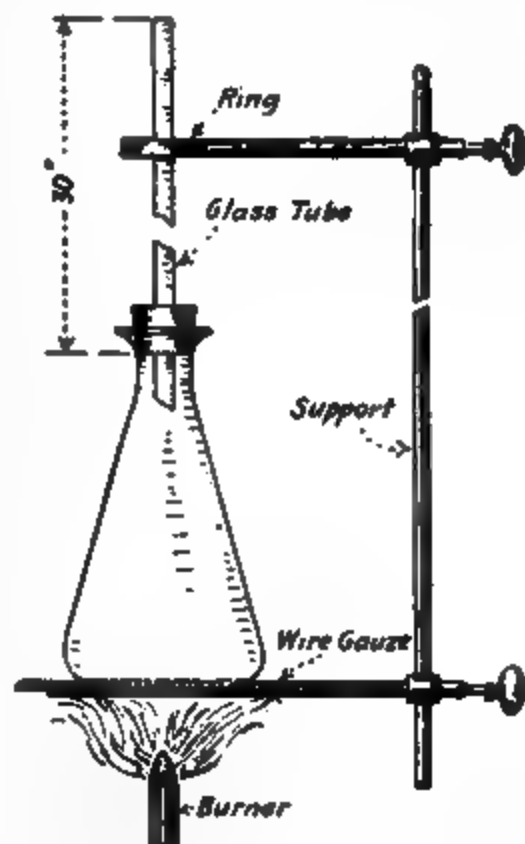


FIG. 102.—Apparatus for Determining Calcium Carbonate with Acid and Alkali.

If the standard sample contains  $L$  per cent carbonate of lime and  $d$  cc. of alkali are required to produce the purple red color, then, to find the carbonate of lime in other samples it is only necessary to subtract the number of cc. of alkali required in their case from  $d$ , multiply the difference by 2, and add to  $L$  for the percentage of carbonate of lime in them; or the number of cc. is greater than  $d$ , subtract  $d$  from this number, multiply by 2, and subtract from  $L$  for the carbonate of lime.

In order to avoid all calculations, prepare a table giving the various percentages of carbonate of lime corresponding to different quantities of alkali.

### Determination

Weigh 1 gram of the sample, which has been ground to pass a 100-mesh sieve, into the flask, add 50 cc. of the standard acid and proceed as directed under standardizing the acid. The percentage of carbonate of lime may be found from the number of cc. of alkali used either from the preceding table or by the formula

$$\text{Per cent CaCO}_3 = L + (d - S) \times 2,$$

where  $L$  and  $d$  have the same values as in the paragraph on "Standardizing the Acid" and  $S$  represents the number of cc. required for the sample whose composition is desired.

### ANALYSIS OF LIMESTONE, CEMENT ROCK, LIME, ROSENDALE CEMENT, ETC.

Dr. Porter W. Shimer, of Easton, Pa., modifies the standard limestone scheme by fusing the sample with half its weight of sodium carbonate. By this means the silicates are decomposed, and yet the quantity of sodium carbonate introduced into the solution is so small that the lime and magnesia precipitates are not contaminated with sodium salts. Below is the method.

**Silica, etc.** Mix thoroughly 0.5 gram of the finely ground sample with  $\frac{1}{2}$  gram of sodium carbonate. Place over a low flame for a few minutes, then gradually raise the flame. Heat over the full flame for five minutes and then over the blast lamp for five minutes. There will be no complete fusion, only a sintering. Put the crucible in a small beaker or casserole and add 30 cc. of water and 10 cc. of hydrochloric acid (sp.gr. 1.10). When the mass is dissolved out of the crucible, rinse the latter off into the beaker and remove any adhering matter with a rubber-tipped rod. To the solution in the beaker or casserole add a little bromine water or a few drops of nitric acid, evaporate to dryness and proceed as directed in the analysis of Portland cement.

For loss on ignition, weigh into a tared platinum crucible 0.5 gram of the sample. Heat at first over a low flame, then gradually raise the temperature and finally ignite over a blast lamp until it ceases to lose weight on reheating. Report such loss in weight as "loss on ignition."

To determine iron and alumina separately, fuse the precipitated ferric oxide and alumina with caustic potash in a silver crucible or dish. Treat with water, boil, and filter. Ignite the residue after washing and weigh as ferric oxide. This weight subtracted from the combined weight of the ferric oxide and alumina gives the weight of the alumina,  $Al_2O_3$ .

To determine alkalies in limestone use the method described for clay, employing 8 grams of the sample and 1 gram of ammonium chloride, but no calcium carbonate.

## CEMENT

Portland Cement	SiO <sub>2</sub>	Insol. M.	Al <sub>2</sub> O <sub>3</sub>	FesO <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	CO <sub>2</sub>	H <sub>2</sub> O	Alkalies, etc.
Typical sample . . . . .	22.0	1.0	7.5	3.5	62.0	1.0	1.5	0.5	0.5	0.5
Extremes . . . . .	18 to 27	—	5 to 10	0 to 7+	58 to 67	0-3	$x$ to 2.75	variable	—	$x$ to 2
Kent-Essex . . . . .	19.62	5.86	10.20	7.44	44.54	2.92	2.61	3.42	0.25	1.46 MnO = 1.57
Natural Cement . . . . .	19 to 28	—	2.5 to 9	1 to 6.5	35 to 62	0.4 to 20	—	CO <sub>2</sub> + Loss = 0.3 to 15 +	—	—

Natural Cement, raw product: See magnesian limestone under raw materials below.

## CEMENT RAW MATERIALS

	Sand	Comb. SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FesO <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	CO <sub>2</sub>	H <sub>2</sub> O	Alkalies and Loss
Chalk . . . . .	0.93	0.43	0.48	—	42.90	0.42	—	34.16	19.03	1.65
Clay . . . . .	28.42	30.30	15.49	7.74	2.04	1.96	1.96	—	12.07	—
Limestone . . . . .	—	0.20	0.08	—	56.02	0.24	—	43.38	0.18	—
Magnesian limestones . . . . .	—	60.22	27.20	—	trace	1.62	—	4.54	—	6.42
Marl . . . . .	—	22.77	10.43	—	34.54	21.85	1.44	2.84	2.50	3.63
Shale . . . . .	—	15.10	7.30	—	42.16	0.34	—	33.51	1.50	—

# METHODS FOR ANALYSIS OF COAL

FRANK E. HALE<sup>1</sup>

Such tremendous value attaches in boiler-room economy to the character of the fuel that the purchase of coal upon the results of laboratory analysis has grown in importance. Specifications have been drawn with such exact requirements that fairness to the coal contractor requires that only exact methods of analysis be employed.

## SAMPLING

In order that the laboratory sample shall be representative of the delivery, great care must be taken, however; the personal element should be eliminated as far as possible. When possible, coal should be delivered by chutes and a shovelful taken at regular intervals throughout the delivery. If delivered in wagons a portion should be taken from each wagon load. Boat loads are best sampled while being loaded or unloaded. If a pile of coal must be sampled, portions should be taken from all sides, top and bottom. The gross sample should preferably be 200 pounds for deliveries up to 100 tons and one-tenth of 1% of the amount delivered for quantities over 100 tons. Larger sizes should be crushed to at least pea size (about  $\frac{3}{4}$  in.) and preferably under. The gross sample should be thoroughly mixed with a shovel, piled up, and quartered. Opposite quarters should then be mixed, piled up, and quartered again and this continued until a sample of about 5 pounds is obtained.<sup>2</sup> This sample should then be forwarded to the laboratory in a sealed moisture-tight container. The most satisfactory container is one made of galvanized iron, to prevent rusting, cylindrical in shape with screw cap flush with the sides. A convenient size is 6 ins. in diameter by 8 ins. height. Such a can is readily cleaned and sealed. Sealing is conveniently made by pasting a strip of paper around the can over the joint, or by means of wax and an impression seal.

## PREPARATION OF SAMPLE FOR ANALYSIS

The laboratory sample should first receive a number which should follow the sample through all phases of preparation in order to avoid confusion. The whole sample, when received at the laboratory, should be crushed to 4-mesh size or less. The Chipmunk Jaw Crusher is rapid and easily cleaned, as one jaw is removable. If too wet to crush, causing clogging of the crusher, the whole sample should be dried on the steam bath, the moisture so lost determined and added to the analytical moisture later determined on the pulverized sample. Shallow agateware pans large enough to take the complete sample are convenient and should set in large holes on the steam bath, so that the body of

<sup>1</sup> Director of Laboratories, Dept. Water Supply, Gas and Electricity, New York City.

<sup>2</sup> The U. S. Bureau of Mines uses a 3-pound sample and New York City a 7-pound sample.

the pan is exposed to the steam and drying is hastened. A few hours only is necessary. The U. S. Bureau of Mines dries in a special oven with a current of dried air at 30-35° C., but this occasions a delay of twelve to ninety-six hours. The crushed sample should be mixed and quartered, preferably by hand. This is best and most rapidly done in the old-fashioned way by raising alternately the corners of a large piece of oilcloth or rubber sheet. The pile may be quickly quartered by two V-shaped pieces of galvanized iron to cut and pull away opposite quarters. The remaining quarters should be again mixed and quartered in the same way and the process continued until a 100-gram representative



FIG. 103.—Illustrates Method of Quartering Coal, Ball Mill for Pulverizing, and Suction Ventilator.

portion is obtained. The discarded quarters should be returned to the can to be retained in case a second analysis is desired. Such check analysis should always be made upon a freshly quartered and pulverized sample of the remaining portions of the original gross laboratory sample.

The 100-gram sample should then be pulverized in an Abbé Ball Mill for three-quarters of an hour. The jar should be nearly full to produce the most rapid pulverization, that is, contain the full charge of pebbles, about 10 pounds for the 9-in. jar. The speed of revolution should be 60 per minute. Natural flint pebbles are least abraded and produce no appreciable effect upon the ash. The ball mill has two distinct advantages. It conserves the moisture



of the coal and it pulverizes so fine that the coal will usually all pass a 60-mesh screen and a large part the 100-mesh screen. This greater fineness prevents incomplete combustion of anthracite coal in the bomb determination to be described later. The pebbles and coal should then be dumped on a cover ash-sifter resting on the oilcloth or rubber sheet, shaken quickly and pebbles and sifter brushed clean. The sample should then be passed through the 60-mesh screen and brushed at once into a moisture-tight container. Any material retained on the 60-mesh screen, which occasionally happens, should be quickly pulverized in a small steel mortar. One-half pint, glass-covered light-tan jars are convenient for containers.

As the dust in coal sampling is so fine as to penetrate through the clothing to the skin, it is wise to use an aspirator to protect the lungs and also use a suction ventilator to keep the air fresh and clean. The suction should connect with small hoods over the crusher and over the quartering table.

## METHODS OF ANALYSIS

**Moisture.** Moisture may be accurately determined on a 10-gram sample heated for one hour at 105° C. Close checks will be obtained and weighing rapid, as the weight need only be taken to the nearest milligram. Glass evaporating dishes of 2½-in. diameter are convenient for this determination. The Beans electric thermo-regulator for gas has been found very satisfactory for oven regulation, as the oven may be heated rapidly and will quickly come to adjustment.

Most laboratories employ a 1-gram sample, however, and later use the residue for ash determination. The Bureau of Mines uses a special drying oven and specially prepared sample for moisture. The 4-mesh sample is crushed in a roll or coffee-mill crusher to 20-mesh, and bottled quickly without sieving.

**Ash.** The ash represents the mineral matter in coal after ignition. No attempt is made in common practice to calculate the original form of the constituents. It is best determined upon a separate portion of coal, and preferably in silica crucibles, as the wear on platinum is considerable. Heating should be slow and careful at first, to avoid loss from volatile matter and avoid the effect of coking. Later the contents should be stirred with a platinum wire to facilitate combustion, not neglecting to tap the wire free from ash. The silica crucibles should rest on silica or nichrome triangles. Some laboratories employ a muffle furnace and others an electric furnace.

The residue from moisture may be used for ash determination, but the residue from volatile combustible matter should not be so used, as there is danger of mechanical loss of ash in the rapid heating, and the accuracy of the ash figure is far more important than the volatile combustible matter.

A 1-gram sample is used for the ash determination.

**Volatile Combustible Matter.** This determination is entirely empirical and should be performed under strictly standard conditions. The determination is made upon a 1-gram sample heated for seven minutes, timed by a stop watch, in a platinum crucible of 25-30 cc. capacity, and with tight-fitting cover. The crucible and cover should be kept brightly polished. A special apparatus should be arranged. Construct a cylinder of asbestos or galvanized iron to protect flame and crucible. Connect an adjustable Méker burner (Scinmat type is preferable) with a U-tube to measure gas pressure. Arrange a platinum

wire from triangle to support the bottom of crucible always at same distance from the burner.

Calibrate the apparatus by adjusting the burner and pressure so that the crucible is entirely surrounded by the flame and the temperature is about  $950^{\circ}\text{C}$ . This may be determined by an optical or other pyrometer, but most conveniently by the fusing-point of potassium chromate. Note the gas pressure required and in the analyses set the gas at this pressure. In this way close checks may conveniently be obtained when the right conditions have been determined.

The loss in weight minus the moisture is the volatile combustible matter.

A 10-20-cc crucible has recently been advocated to reduce the effect of oxidation by oxygen in the crucible. Several different schemes have been advocated in order to obtain uniform results. An electric furnace is used by some. Any method is empirical, as the determination does not represent any

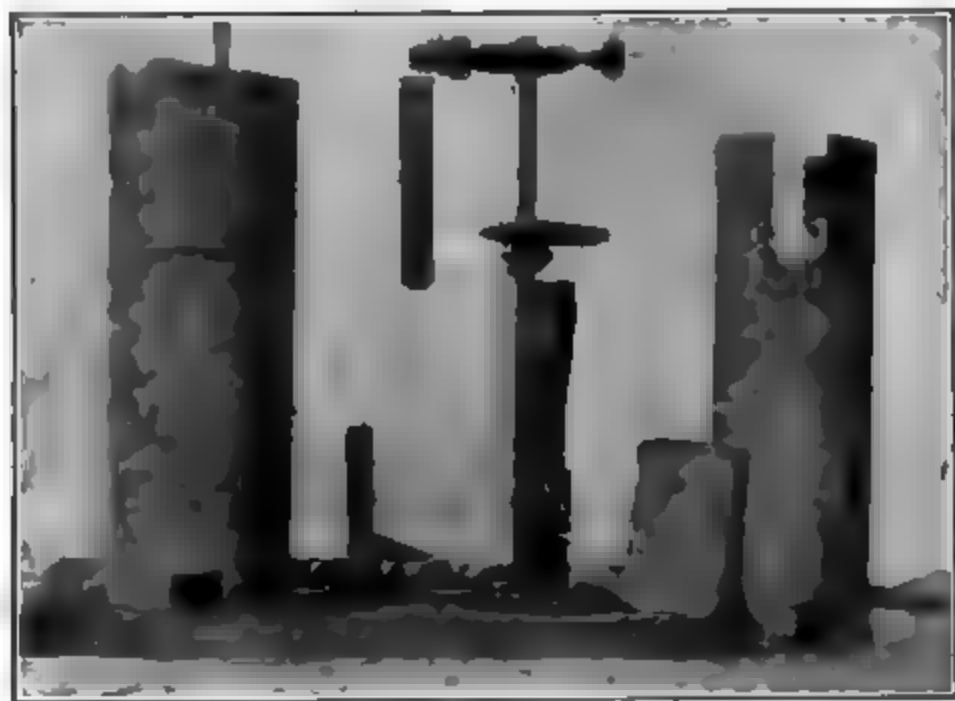


FIG. 104.—V. C. M. Apparatus

Very definite constituent of the coal. Originally intended as a measure of coking ability the V.C.M. is now mainly a means of discriminating between different kinds of coal and as a means of keeping within the smoke ordinances.

**Volatile Sulphur.** The total sulphur in a coal is of little importance. If desired, it may be determined by the well-known Eschka method. The volatile sulphur is of great importance both in its bearing upon fusibility by indicating the presence of pyrites in the coal and in its relation to corrosion by the formation of sulphurous acid.

Volatile sulphur is determined in the bomb washings after a calorific determination. These washings are filtered if necessary and titrated for acidity for one of the corrections in the calorific calculation. The sulphur is then determined most rapidly and conveniently by a Jackson Candle Turbidimeter.

"The titrated solution is made up to 200 cc. The amount of acidity found is used as a guide in selecting the aliquot for the sulphur determination. In

## TURBIDIMETRIC SULPHUR TABLE

For use with Jackson's candle turbidimeter  
Sulphur and SO<sub>2</sub> contained in 100 cc. precipitated

Depth. Cm.	S. Mg.	SO <sub>2</sub> . Mg.	Depth. Cm.	S. Mg.	SO <sub>2</sub> . Mg.	Depth Cm.	S. Mg.	
1 0	20 0	50.0	5.0	3 66	9 15	9 0	2.30	4
1 1	18.0	45 0	5.1	3.60	9 00	9.1	2 28	4
1 2	16.5	41.3	5 2	3.54	8.85	9.2	2.26	4
1 3	15 0	37 5	5 3	3.49	8.73	9.3	2.25	4
1.4	13 5	33 8	5 4	3.43	8.58	9 4	2.23	4
1.5	12.5	31.3	5.5	3.38	8.45	9 5	2.21	4
1 6	11 2	28.0	5.6	3.33	8.33	9.6	2.19	4
1.7	10 0	25.0	5 7	3.28	8.20	9.7	2 18	4
1 8	9.5	23 8	5.8	3 24	8 10	9.8	2 16	4
1 9	9.0	22.5	5.9	3.20	8.00	9.9	2.15	4
2 0	8.5	21.3	6.0	3.15	7.88	10.0	2.13	4
2 1	8.0	20.0	6.1	3.11	7.78	10.1	2.11	4
2.2	7.6	19 0	6.2	3.07	7 68	10.2	2.10	4
2 3	7.3	18 3	6.3	3.03	7.58	10.3	2.09	4
2 4	7.0	17.5	6.4	2.99	7.48	10.4	2 07	4
2 5	6 7	16.8	6 5	2.95	7.38	10 5	2.06	4
2 6	6 5	16.3	6.6	2.92	7.30	10 6	2.04	4
2.7	6 3	15 8	6.7	2.88	7.20	10 7	2.03	4
2 8	6.1	15.3	6 8	2.85	7.13	10.8	2 02	4
2 9	5 9	14.8	6.9	2.82	7.05	10 9	2 01	4
3 0	5 7	14 3	7 0	2.79	6.98	11 0	2 00	4
3 1	5 5	13.8	7 1	2 76	6.90	11.1	1 98	4
3 2	5 4	13 5	7.2	2.73	6.83	11.2	1 97	4
3.3	5 2	13.0	7.3	2.70	6.75	11.3	1 95	4
3.4	5 1	12 8	7 4	2 67	6 68	11 4	1.94	4
3 5	5 0	12 5	7.5	2 64	6.60	11.5	1.93	4
3 6	4 85	12 25	7.6	2.61	6.53	11.6	1 92	4
3.7	4 75	12 00	7.7	2 59	6 48	11.7	1.91	4
3.8	4.63	11 75	7.8	2.56	6.40	11.8	1.90	4
3 9	4.52	11 50	7.9	2.54	6.35	11.9	1.89	4
4 0	4.43	11.25	8.0	2.51	6.28	12.0	1.88	4
4 1	4.33	11 00	8.1	2.49	6.23	12 1	1.87	4
4.2	4.24	10 75	8.2	2.47	6.18	12.2	1.86	4
4.3	4 16	10 50	8 3	2 44	6 10	12.3	1 85	4
4 4	4 08	10 25	8.4	2.42	6.05	12 4	1.84	4
4 5	4 00	10 00	8 5	2.40	6.00	12 5	1 83	4
4 6	3.93	9 83	8 6	2.38	5 95	12.6	1.82	4
4 7	3 86	9 65	8.7	2.36	5 90	12.7	1.81	4
4.8	3 79	9.48	8.8	2.34	5 85	12 8	1 80	4
4 9	3.72	9 30	8.9	2 32	5 80	12 9	1 79	4

TURBIDIMETRIC SULPHUR TABLE.—*Continued*

Depth. Cm.	S. Mg.	SO <sub>2</sub> . Mg.	Depth. Cm.	S. Mg.	SO <sub>2</sub> . Mg.	Depth. Cm.	S. Mg.	SO <sub>2</sub> . Mg.
13 0	1 78	4 45	17.1	1 49	3 73	21.1	1 24	3 10
13 1	1 77	4 43	17 2	1 49	3 73	21 2	1 23	3 08
13 2	1 76	4 40	17 3	1 48	3 70	21 3	1.23	3 08
13 3	1 75	4 38	17 4	1.47	3.68	21.4	1 22	3 05
13 4	1.74	4.35	17.5	1 47	3.68	21 5	1.21	3 03
13 5	1 73	4 33	17 6	1.46	3 65	21 6	1 21	3 03
13 6	1 73	4 33	17 7	1 45	3 63	21.7	1 20	3.00
13 7	1 72	4 30	17 8	1 44	3 60	21 8	1 20	3 00
13.8	1 71	4 28	17.9	1 44	3 60	21 9	1.19	2 98
13 9	1 70	4 25	18 0	1 43	3 58	22 0	1.18	2 95
14 0	1 70	4 25	18 1	1 43	3 58	22.1	1.18	2 95
14 1	1 69	4 23	18 2	1.42	3.55	22.2	1 17	2.93
14 2	1 68	4 20	18 3	1 41	3 53	22 3	1 16	2 90
14 3	1 67	4 18	18 4	1 41	3 53	22 4	1.16	2.90
14 4	1 66	4 15	18 5	1 40	3 50	22 5	1.15	2 88
14 5	1 66	4 15	18.6	1.40	3 50	22 6	1.15	2.88
14 6	1 65	4 13	18.7	1 39	3 48	22.7	1 14	2.85
14 7	1 64	4 10	18 8	1 38	3.45	22 8	1.13	2 83
14 8	1 63	4 08	18 9	1 38	3 45	22 9	1 13	2 83
14 9	1 62	4 05	19.0	1 37	3 43	23 0	1 12	2 80
15 0	1 62	4 05	19.1	1 37	3 43	23 1	1.11	2.78
15 1	1 61	4 03	19 2	1 36	3 40	23 2	1 11	2.78
15 2	1 60	4 00	19 3	1 35	3 38	23 3	1.10	2.75
15 3	1 60	4 00	19 4	1 35	3 38	23 4	1.09	2.73
15 4	1 59	3 98	19 5	1 34	3 35	23.5	1 08	2.70
15 5	1 59	3 98	19 6	1 34	3 35	23 6	1 08	2.70
15 6	1 58	3 95	19 7	1 33	3 33	23.7	1.07	2.68
15 7	1 57	3 93	19 8	1 32	3 30	23.8	1 06	2.65
15 8	1 57	3 93	19 9	1 32	3 30	23.9	1 05	2.63
15 9	1 56	3 90	20 0	1 31	3 28	24 0	1.05	2 63
16 0	1 56	3 90	20 1	1 30	3 25	24 1	1 04	2.60
16 1	1 55	3 88	20 2	1 30	3 25	24 2	1 03	2 58
16 2	1 54	3 85	20 3	1 29	3 23	24 3	1.03	2.58
16 3	1 54	3 85	20 4	1 28	3 20	24 4	1.02	2.55
16 4	1 53	3 83	20 5	1 28	3 20	24 5	1.02	2.55
16 5	1 53	3.83	20 6	1 27	3.18	24 6	1.01	2.53
16 6	1 52	3 80	20.7	1.26	3.15	24.7	1 01	2.53
16 7	1 52	3 80	20 8	1 26	3.15	24.8	1 00	2.50
16 8	1 51	3 78	20 9	1 25	3 13	24 9	1.00	2 50
16 9	1 50	3 75	21 0	1 25	3 13	25 0	1 00	2 50
17 0	1 50	3 75						

the case of anthracite coals, the amount taken is one-fourth to one-half; in the case of soft coals from one-fourth to one-tenth of the whole."

"The aliquot of the solution to be tested is measured into the turbidimeter tube, diluted to near the 100-cc. mark, shaken, then acidified with 1 cc. of 1 : 1 hydrochloric acid, made up to the mark, and mixed well by shaking. A barium chloride tablet<sup>1</sup> weighing 1 gram and compressed without the use of a binder is then dropped in and the tube closed by means of a clean rubber stopper. The tube is then tilted up and down, causing the tablet to roll back and forth through the solution by gravity.

When the precipitation appears to be complete, the remainder of the tablet may be dissolved by rapidly rotating the tube; but violent shaking should be avoided, since it would have a tendency to cause aggregation of the precipitate. The turbid liquid is then transferred to a beaker, the candle lighted, a small quantity of the liquid poured into the glass tube to prevent overheating and cracking, and the tube put in place. More of the liquid is then poured in, allowing it to run down the side of the tube, rapidly at first, until the image of the flame becomes dim, then more slowly, waiting a moment after each addition until the liquid in the tube is quiet, and continuing thus until the image of the flame just disappears. The depth of the liquid in centimeters is noted. The mixture is then returned to the beaker, poured back and forth from beaker to tube two or three times, and read again as before.

"The precipitated solution is read at least twice, and the readings usually check exactly, unless they fall in the upper part of the tube, where they may differ by a centimeter without materially altering the results. In this case readings may be averaged. The amount of sulphur corresponding to the depth of liquid in the tube is found in the table, and multiplied by the proper factor, depending on the aliquot of the original solution taken.

"All dilutions must be made before precipitation, for otherwise the results will not be concordant for different dilutions." The average time required is ten minutes or less. The method carried out as described is accurate to about 0.05% sulphur.

**Fixed Carbon.** Fixed carbon is found by adding the moisture, ash, and volatile matter together, and subtracting from 100%.

**Calorific Value.** Heat value is expressed as "small calorie (cal.)," the amount of heat required to raise the temperature of 1 gram of water 1° C., "large calorie (Cal.)," the amount of heat required to raise the temperature of 1 kilogram of water 1° C., and "British thermal unit (B.t.u.)," the amount of heat required to raise the temperature of 1 pound of water 1° F., at or near 39.1° F. Small calories per gram of coal multiplied by 1.8 equal B.t.u. per pound of coal.

It is preferable to express results as B.t.u. per pound of dry coal, instead of coal as received, since comparison between different samples of coal and the results of different analysts and laboratories are facilitated. The other determinations except moisture are also better expressed on the dry basis.

<sup>1</sup>These tablets are prepared on order by the Fraser Tablet Co., of Brooklyn, N. Y., Formula No. 188,603.

On standing for some time, some of the tablets become coated with a thin layer of effloresced salt. This should be removed by gently rubbing between the fingers before using the tablet. It is not advisable to keep the tablets in a moist atmosphere to prevent this efflorescence, as they become extremely hard and difficult to dissolve.

As a check upon accuracy of work and to catch errors, results of B.t.u. should also be calculated to B.t.u. per pound of combustible, that is, divide the B.t.u. dry basis by (100% minus the per cent of ash). For the same run of coal, this value changes but little, usually within 200 B.t.u.

The calorific determination should be made by means of a bomb calorimeter. The platinum-lined Atwater type is convenient. The Emerson is more commonly used in this country.

Unfortunately the Atwater bomb is no longer manufactured, although it is still used by laboratories possessing it. The Emerson bomb calorimeter is an excellent type available in the American market.

One gram of the 60-mesh sample of coal prepared for analysis is weighed into a nickel capsule (28 mm. top width, 23 mm. bottom width, and 12 mm.

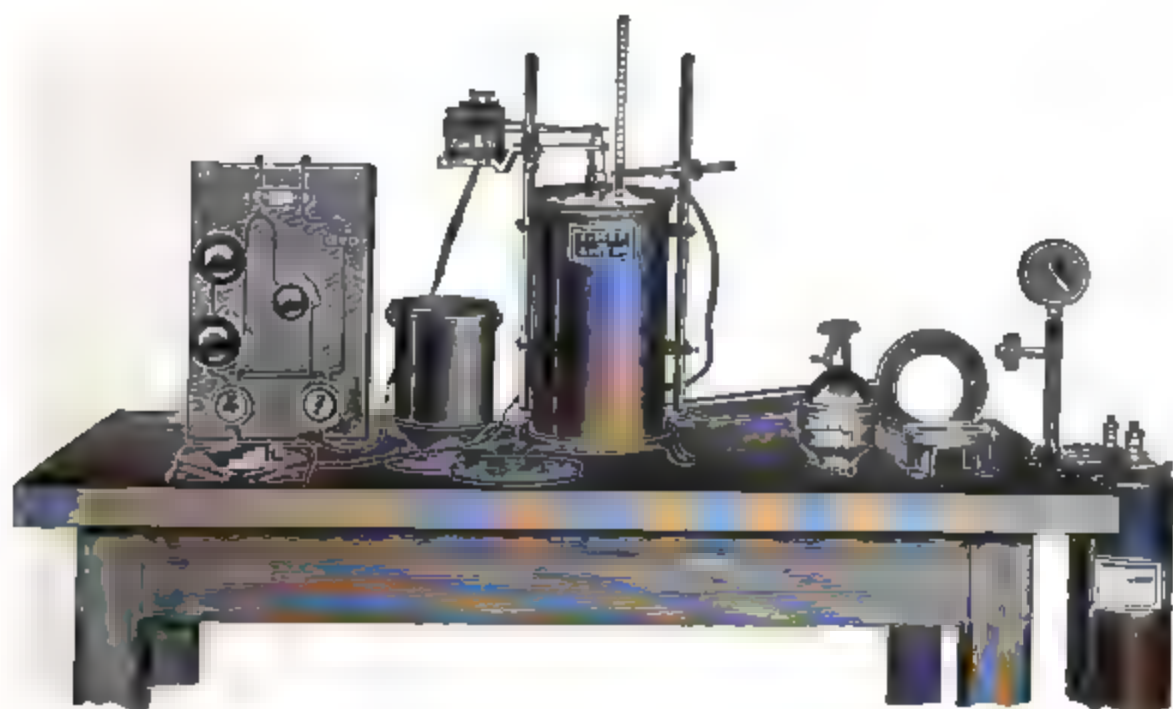


FIG. 105. Emerson Calorimeter and Accessories.

depth) in the bottom of which has been placed an ignited disc of asbestos paper. The latter prevents incomplete combustion of anthracite coal by preventing chilling of the coal after combustion starts. In weighing large numbers of samples a piece of tared platinum foil is convenient and the coal transferred with a camel's-hair brush into the nickel capsule. The capsule is supported on a platinum ring suspended by a platinum wire from the head of the bomb. A piece of iron fuse wire, No. 34 B. & S. gauge, and weighing 10 milligrams, is attached at one end to the wire supporting the tray and at the other end to another platinum wire extending downward from the head, but insulated from it. Attachment of the fuse wire is made by winding around the platinum wires several times. The center of the fuse wire should dip into the coal slightly. A convenient method of obtaining pieces of fuse wire of uniform weight is to wind around a flat piece of board or cardboard and cut the loops.

The shell of the bomb is rinsed with water and sufficient moisture, one-half cc., is thus left to take up the acids formed by combustion. The head is next joined gas tight to the shell of the bomb by the collar. Lead gaskets render these joints tight. Oxygen gas is slowly introduced, so as not to blow the coal out of the pan, until about 21 atmospheres pressure is recorded in the bomb. The needle valve is then closed just tight enough to prevent leakage, the valve on oxygen tank closed and the bomb disconnected. Twenty atmospheres pressure should remain in the bomb for the combustion, an amount

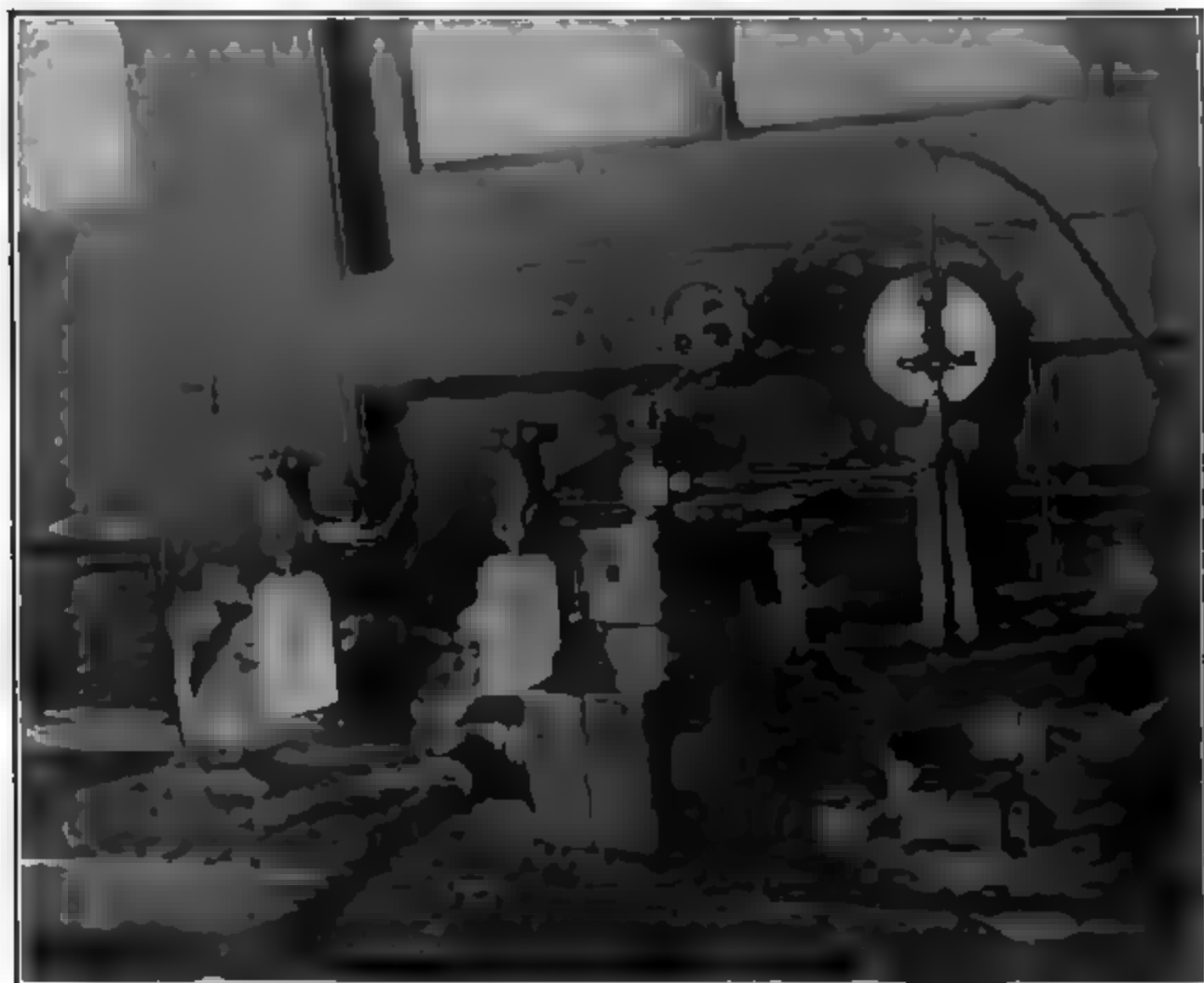


FIG. 106.—Illustrates Method of Connecting Two Oxygen Cylinders for Filling Bomb when Pressure in One is below Twenty Atmospheres.

sufficient for complete combustion of the coal and an amount containing sufficient nitrogen together with the nitrogen in the air trapped in the bomb to cause the sulphur to burn to sulphuric acid completely, unless the sulphur is unusually high.

The bucket is filled with enough distilled water, about 3° C. below the room temperature, to make the water equivalent of the calorimeter some round number, i.e., 2000 g. with Atwater, 2900 g. with Mahler, or 2350 g. with Emerson. The water is best weighed on a balance, capable of delicacy with such heavy weights, and the amount of water should be sufficient to cover the bomb. The bomb is placed in its support and placed in the water in the bucket. The latter is set in the calorimeter, the stirrer added so as not to touch bomb or bucket,



covers applied and thermometer placed in the water and adjusted so that it can be read during the combustion. The thermometers should be special and standardized by the Bureau of Standards. The Fuess type of Beckmann is excellent.

Connect the poles of six dry cells to the stem and insulated post of the bomb. Connection should be made with a button for firing the coal. It is also convenient to have a small electric lamp connected with the button to indicate that the batteries are in condition, before a run is started.

The calorific determination should be made in a room protected from sudden changes of temperature and from draughts. If a current of air strikes the thermometer during a determination, the results will be untrustworthy. Mechanical stirring is preferable and should be at a moderate rate. The stirrer is started and after a couple of minutes or so, when conditions have become uniform, the thermometer is read by means of a telescope and readings taken every one-half minute for six readings. Interpolate to the  $0.001^{\circ}\text{C}$ . A clock striking every half minute is convenient. After the sixth reading, fire the coal by pressing the button connected with the batteries and take approximate readings of the thermometer every half minute, reading to the  $0.001^{\circ}\text{C}$ , as soon as the rise is slow enough to do so. After the maximum temperature has been reached, take six more readings at half-minute intervals.

Remove the bomb from the bucket and allow the gas to escape slowly. Disconnect the head and rinse out the bomb thoroughly. Titrate the washings with  $\text{N}/10$  sodium carbonate, using methyl orange as indicator. Determine the sulphur, after titration, with the turbidimeter as under Volatile Sulphur.

**Calculation of B.T.U.** The table on page 1226 is an example of an actual determination, showing corrections as applied.

Corrections must be applied to the thermometer in accordance with the certificate furnished for each thermometer by the Bureau of Standards, including the correction for temperature of setting of Beckmann thermometers and emergent stem correction for others.

The thermometer should also be fitted with a vibrator to overcome meniscus error. This is conveniently done by arranging a small electric vibrator so that the hammer hits the rubber-covered metal clamp supporting the thermometer. The vibrator should, of course, be connected to a push-button and dry batteries.

Correction must also be made for changes of temperature due to radiation. A simple formula which yields results within  $0.002^{\circ}\text{C}$ . as compared with the more elaborate formulae is the following:

$$\frac{x(a+b)}{2} + yb = \text{radiation correction.}$$

$a$  = average preliminary period change per half minute;

$b$  = average final period change per half minute;

$x$  = number of half-minute intervals of combustion period during which the rise of temperature (expressed to the nearest  $0.01^{\circ}$ ) was greater than 10% of the total rise. This is readily seen by inspection;

$y$  = remaining number of half-minute intervals of combustion period.

The algebraic signs must be observed in the formula.



The end of the combustion period is taken as the first reading after the maximum temperature. The reason for this rests in the fact that the real maximum rarely occurs at a half-minute interval reading, as shown by a drop, during the first period after the maximum temperature read, of less than the

## NO. 1 BUCKWHEAT COAL

Thermometer used ( $T_1$ ), zero set at 20.4° C.

Room Temperature 22.5° C. Atwater bomb.

Acid found equal 7.2 cc. N/10  $\text{Na}_2\text{CO}_3 \times 1.45 \text{ cal.} = 10.4 \text{ calories}$

Volatile sulphur (aliquot  $\frac{1}{2}$ ) 8.6 cm. = .0048 gram  $\times 13 \text{ cal.} = 6.2 \text{ calories}$

Iron wire (10 milligrams) = 16.0 calories

32.6 calories

Thermometer readings, Half minute intervals			
Preliminary period	0.979	Corrected temperature, end of combustion period . . . . .	4.277
	0.980	Corrected temperature, end of preliminary period . . . . .	0.986
	0.981		
	0.983	Apparent rise in temperature corrected for thermometer calibration. . . . .	3.291
	0.984	Thermometer correction for setting and room temperature . . . . .	+0.022
	0.986		
Average rise in temperature: $\frac{.007}{5} = .0014$		Apparent rise in temperature, corrected for thermometer setting. . . . .	3.313
Combustion period	1.800	Radiation correction: $3 \left( \frac{(-.0014) + (+.0036)}{2} \right) + 5(+.0036)$	+0.021
	3.270		
	4.050	Corrected rise in temperature . . . . .	3.334
	4.225	Water equivalent (grams) . . . . .	2000
	4.267	Calories ( $2000 \times 3.334$ ) . . . . .	6668.0
	4.278	Correction for acidity, sulphur trioxide and iron. . . . .	32.6
Final period	4.279	Actual calories, coal as received. . . . .	6635.4
	4.278	Calories (dry basis) $6635.4 + .9522 (100\% - \text{moisture})$ . . . . .	6968.5
	4.273	B.t.u. per lb. of coal (dry basis) ( $6968.5 \times 1.8$ ) . . . . .	12,543
	4.270	B.t.u. per lb. of combustible (dry basis) $12543 \div .842 (100\% - \text{ash})$ . . . . .	14,897
	4.268		
Average fall in temperature: $\frac{.018}{5} = .0036$			
B.T.U. . . . . 12,543			
V.C.M. . . . . 7.7 %			
Ash . . . . . 15.8			
Vol. sulphur . . . . 0.48			
Moisture . . . . . 4.78			

average final change. Correcting for an extra combustion interval counteracts this error.

The nitrogen in the coal and in the air of the bomb forms nitric acid. This does not occur when coal is burned in the furnace, hence the bomb determination is too high by the amount of heat thus produced. The calorific value of nitrogen burning to nitric acid is 230 calories per gram of nitric acid. Each

cubic centimeter of N/10 sodium carbonate used in the titration represents 1.45 calories.

Furthermore, sulphur in the furnace burns to the dioxide and in the bomb to the trioxide. This excess heat in the bomb must be corrected for as well as the fact that all of the above acidity is not nitric, but is partly sulphuric acid. This correction is conveniently made by adding to the acidity correction (made as if it were all nitric acid) 13 calories for each 0.01 gram of sulphur. This represents the excess which the oxidation correction is over its expression as the formation of nitric acid as obtained from the titration.

The correction for the iron fuse wire is 16 calories for each 10 milligrams.

All other corrections are met by standardization under conditions similar to those under which the calorimeter is to be used. Such errors arise from loss of heat by evaporation of water while stirring (probably covered by the radiation correction), gain in heat due to combustible gases in the oxygen, changes in specific heat of water at various temperatures, changes in the gases present after combustion, and changes of pressure of the gases in the bomb. The last three errors are too small to take into account. The oxygen error has disappeared since the introduction of the purer gas manufactured by the Linde Air Products Company.

Inspection of the bomb contents should always be made to insure that there are no sooty deposits or coal thrown from the capsule. Some coals require to be compressed into pellets to prevent the above.

The procedure outlined above, using half-minute intervals, saves considerable time (nearly one-half) over the usual procedure and produces very accurate results.

**Standardization of the Calorimeter.** While there are several ways of determining the water equivalent of the calorimeter, that is, the heat capacity of the apparatus expressed as though it were all water, only one method should be used by commercial laboratories, and that is to burn in the calorimeter a known weight of pure substance, the calorific value of which has been determined by the Bureau of Standards, Washington, D. C. Of those furnished, benzoic acid is preferable, as it readily ignites and burns completely. If cane sugar should be used, a few milligrams of benzoic acid are necessary to assist ignition and correction must be made for its heating value. Cane sugar does not always burn completely.

Procure standardized benzoic acid from the Bureau of Standards. Compress into pellets by means of pellet press sufficient benzoic acid to produce approximately as many calories as are given by the coal, that is, about 7000 calories. One gram of benzoic acid produces 6320 calories. Determine in the calorimeter the temperature rise produced by the benzoic acid with the precautions used in a regular coal analysis, correcting for thermometer and radiation errors. Multiply the grams of benzoic acid taken by 6320 calories, add the calories produced by formation of nitric acid as obtained from the titration and add the calories produced by the iron fuse wire. Divide this sum by the corrected rise in temperature. The quotient is the water-equivalent of the calorimeter. The amount of water added to the bucket is then changed so as to make the total calorimeter equivalent a round number, such as 2000 for the Atwater or 2900 for the Mahler, or 2350 for the Emerson. The water should entirely immerse the bomb and avoid spattering by the stirrer. Then restandardize with the new quantity of water. The conditions of combustion should be as closely as possible like those prevailing during regular coal analysis.

### DETERMINATION OF FUSIBILITY OF COAL ASH

This determination has become of increasing importance in recent years especially in relation to mechanical stokers and gas manufacture. The composition of the ash, not its amount, is the determining factor. Alumina, the most refractory constituent and its fusing-point,  $2000^{\circ}\text{C}$ ., is lowered propor-



FIG. 107.—Hoskins Electric Furnace, Optical Pyrometer in Position. Also (X) Method of Supporting Cone in Graphite Block.

tionately to the amounts of silica, alkalies, and iron present. In many coals the amounts of all but the latter do not lower the fusing-point sufficiently to cause trouble, that is, below  $1400^{\circ}\text{C}$ . The amount of iron becomes then of supreme importance, as the last straw that breaks the camel's back. This is popularly shown in the classification of coals as red ash and white ash. The

condition of the iron is of great importance also, as in the ferric condition it has but slight effect, but in ferrous condition it lowers the fusion-point greatly. The influence of sulphur upon fusing-point probably depends upon the accompanying presence of iron as pyrites. In the coal bed in the presence of burning carbon the ferric oxide may be reduced to ferrous oxide or not, according to the care of the fire and the amount of oxygen supplied. This explains discrepancies occurring between the facts of clinkering of the coal on the grates and the fusing-point as determined in a laboratory furnace. The fusing-point varies in different types of furnaces for the same reasons. It seems safest to choose such furnaces in laboratory tests as give reducing atmospheres and hence lower fusing-point, indicating the possible danger.

A convenient furnace, for high temperatures especially, is the Hoskins Electric Furnace. The heat is generated by passing a heavy alternating current of low voltage through a series of carbon plates. Temperature is regulated by compression of these plates. This furnace uses a 60-cycle alternating current, 220 volts, about 40 amperes. The current is transformed by an air-cooled transformer to a current of 10 volts. The maximum temperature produced by the furnace is about 2000° C.

The coal is burned to ash at as low a temperature as possible in clay dishes. The ash is moistened with water and moulded into the shape of a Seger cone ( $\frac{1}{4}$  in. by  $2\frac{1}{4}$  ins.) by pressing into a mould conveniently made of lead. A piece of thin paper, moistened, is laid in the mould to facilitate removal of the cone. Some coals may require 10% dextrin paste as a binder, but it is usually unnecessary. The use of smaller cones has recently been advocated. The cones may be set in triangular holes in a Dixon graphite block and placed in the furnace so that the cone is horizontal. This position gives as concordant results as the vertical position, if not closer. The fusing-point is taken when the cone droops into a vertical position. The temperature must not rise too rapidly when near the fusing-point, about 5° C. per minute. The temperature is conveniently read by a fixed-focus total-radiation pyrometer or an optical pyrometer of the Wanner type. Reducing atmospheres preclude the use of metallic couples at high temperatures.

NOTE. The methods in this chapter are based upon those in use at the Mt. Prospect Laboratory, of the Department of Water Supply, Gas and Electricity, New York City. The method for fusibility was obtained originally from the Laboratory of the Consolidated Gas Company, New York City.

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# GAS ANALYSIS

AUGUSTUS H. GILL<sup>1</sup>

## SAMPLING

The process<sup>2</sup> consists in the insertion of a suitable tube into the flue or duct, and the withdrawal of the gas sought, by some sort of pump.

**Tubes.** The tube employed varies with the nature of the gas and its temperature. Ordinarily, a combustion tube a meter long of 16-17 mm. outside diameter, which has been drawn down to 7 mm. at one end, to facilitate the attachment of rubber tubing, is used. These soften at about 500° C. For higher temperatures we have a choice of quartz, porcelain tubes of about the same dimensions, or water-cooled metal tubes. Uncooled metal tubes cannot be employed above 250° without danger of reduction of the oxides of the metals composing the tube, by the carbonic oxide contained in the gases.<sup>3</sup> If porcelain



FIG. 108.

tubes be used, they should be glazed within and without, to prevent the trans- fusion through them of the lighter gases like methane and hydrogen: they, as well as glass tubes, should be warmed before insertion into a hot flue. The construction of the water-cooled tubes will be evident from Fig. 108.

For cooling the gas, the tube should not be inserted to its full length. Rolls of wire gauze can be inserted near the cool, drawn-out end of the tube: these will serve for the removal of soot and dust. The removal of dust may be further effected by the use of plugs of asbestos or glass wool.

The place from which the gas is collected should be so chosen as to give a representative sample, and all openings except those intended for the inlet of air, stopped up. In a circular duct or chimney the average velocity of the gases is usually at a point one-third the distance from the wall to the center. In case of a boiler, the setting should be carefully inspected, all cracks filled with mortar, and the clean out doors made tight. The fact that bricks themselves are porous must not be lost sight of, and new settings should be sized and given a coat of whitewash. If possible the tube should be inserted below the damper to avoid

<sup>1</sup> Professor of Technical Analysis, Massachusetts Institute of Technology.

<sup>2</sup> See also Bureau Mines Bulletin, No. 97, "Sampling and Analyzing Flue Gases."

<sup>3</sup> Fischer, "Technologie der Brennstoffe," 1880, p. 221, cites an instance in which CO<sub>2</sub> was changed from 1.5 in the mixture, to 26% by the passage through an iron tube heated to dull redness.

leakage from that source. A second hole should be made for the introduction of an oil tube for the thermometer. The joints around these tubes should be made tight with mortar, plaster of Paris, or in the case of a temporary connection, putty or wet cotton waste. Care should be taken not to insert the tube so close to the source of heat as to withdraw the gases in a dissociated or partially decomposed condition. For sampling the gases from different zones of a blast furnace, water-cooled tubes are made which can be screwed together to produce the desired length.

**Pumps.** Where a sufficient head of water (15 or 20 lbs. is enough for our purpose) is available, the Richards jet pump, Fig. 109, may be used. This can be

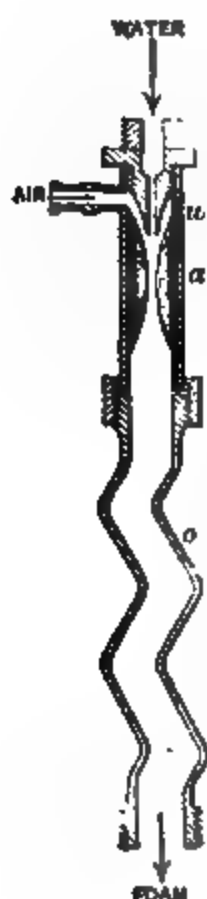


Fig. 109.

easily constructed in glass as shown in Fig. 110 and the glass jets drawn down to suit the water pressure. It may be noted that the pump may be operated with steam equally as well as with water.

In case a head of water be not accessible, pumps employing a fall of water—the Bunsen pump, Fig. 111, may be used. This consists essentially of a quarter-inch tee, one branch of which is connected with the water supply, another with the vessel to be evacuated, while the third is connected with 10<sup>1</sup> or 15 ft. of quarter-inch pipe, preferably lead. The water in this acts as a moving piston and draws the gas in after it.



Fig. 110.

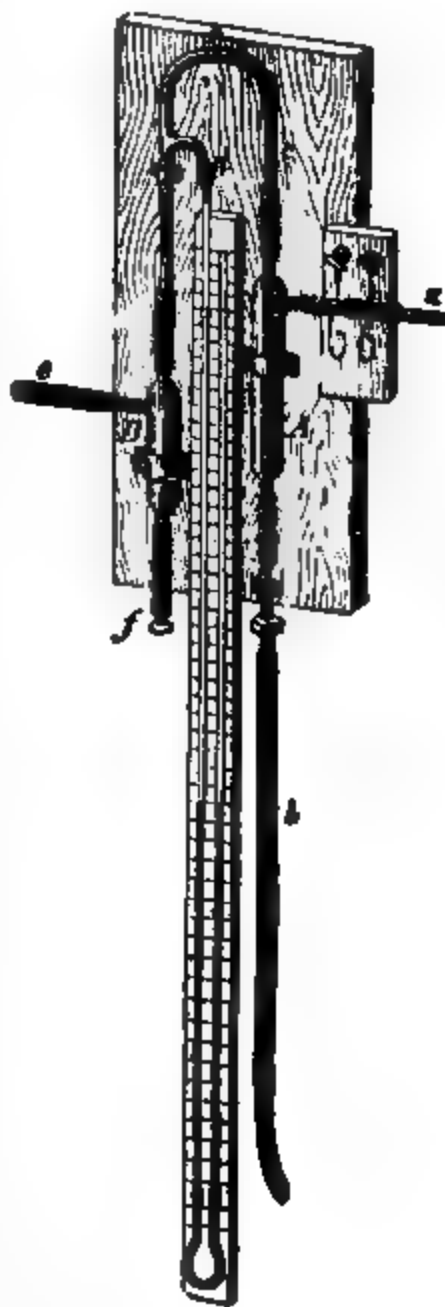


Fig. 111.

Where none of these is available, some type of a power-driven pump, or an ordinary rubber syringe bulb may be employed. Instead of these, two aspirator bottles—of gallon or two-gallon size—will furnish the necessary suction. These are made by passing two glass tubes bent at right angles through each rubber stopper fitting the bottles: one branch of one elbow stops just under the stopper, while a branch of the other goes to the bottom of the bottle. The tubes carrying the long branches are connected by a 3- or 4-foot piece of quarter-inch rubber tubing provided with a screw pinch-cock. Upon setting one bottle higher than the other and blowing into its shorter tube, water siphons through the longer into the lower bottle, producing suction in the upper. This is sometimes used for taking a continuous sample extending

<sup>1</sup> For the highest vacuum over 32 ft—the height of the water barometer.

over several hours. Strong brine is a suitable solution for the bottles, since it possesses the advantage over water in absorbing less carbon dioxide.

**Containers for Samples.** These are of glass, preferably of the shape shown in Fig. 112. Being pear shaped, the vessel is completely emptied, leaving no liquid to exercise a solvent action on the gas. The tubing shown in the figure is of lead, which can be safely used for chimney gases after it becomes attacked by them. Its obvious advantage is found in the fact that it bends rather than breaks. Glass bottles—parts of the aspirator just described—may be used; the rubber connection should be thick, carefully wired on and provided with screw pinch-cocks. The long tube should carry a short piece of rubber tubing within the bottle reaching to its side; by tipping it the water can be more completely run out through this tube. The use of metal containers in general is not recommended, as those of zinc or galvanized iron are attacked by carbon dioxide; where the gases do not act upon the metals they may of course be advantageously employed. To ensure tightness, the rubber stoppers used should be held in by screws which fit into a brass plate on top of the stopper and into wire loops about the neck of the bottle. This compresses the stopper about the tubes and into the bottle neck, making a thoroughly tight joint. Or the brass plate may be replaced by a piece of sole leather and wire passed over this after the manner of wiring down the bottles containing carbonated waters.

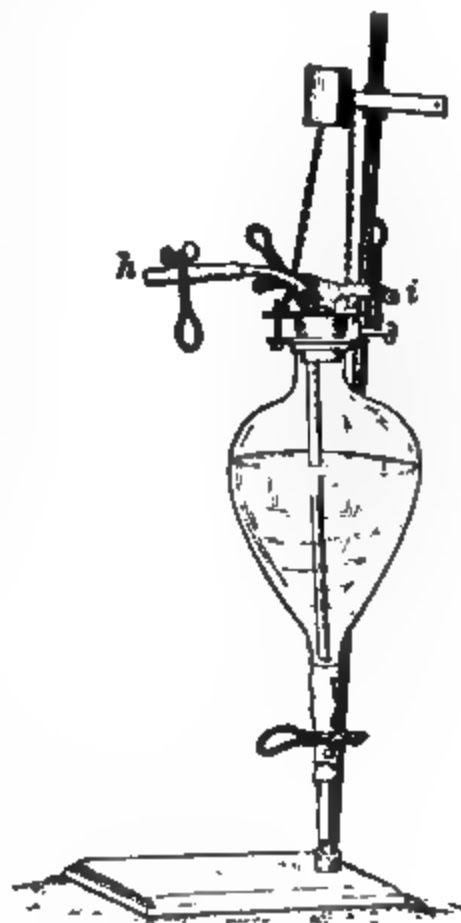


FIG. 112.

The use of rubber bags is not to be recommended, as they absorb certain gases and are oxidized by others: the most satisfactory containers are glass tubes provided with drawn-out ends which can be sealed in the lamp flame.

In connecting up the sampling tube, container and pump, the use of rubber tubing is to be avoided as much as possible for the reason just given.

## MEASUREMENT OF GAS IN LARGE QUANTITIES. METERS

Several types of instruments are available for this purpose.

The wet meter	} Measure total gas passed—not for acid gases.	
The dry meter		
The Pitot tube or Davis anemometer	} All these measure velocity simply	} For all gases particularly acid
The Rotameter or Thorp gauge		
The Capometer		
The Thomas electric meter		
The orifice meter		
The anemometer		

The first two meters show all the gas passing through the system while the others simply measure the rate of flow: with these the size of the pipe must be



known. Of all these instruments, the wet meter and Thomas meter are probably the most accurate. They, however, like some of the others, cannot be used with corrosive gases, being constructed of metal; hence the Pitot tube, rotameter and capometer are the ones to be employed in chemical works.

The wet meter consists of a cylindrical drum divided into four spiral compartments, suspended in a bath of water, surrounded by a tight casing: the pressure of the gas causes the drum to rotate, emptying a drumful of gas into the casing and pipes. It must be set level, the water level carefully adjusted to the mark on the glass gauge, with its top open, as well as the inlet and outlet pipes of the meter. The higher the water level the faster the meter. The dry meter consists of a pair of metal bellows, with sides of leather soaked in oil, on either side of a diaphragm, and connected with slide valves so that a bellowsful of gas is alternately emptied into the upper part of the meter and piping. The vibrations of the bellows produced by the gas pressure are transmitted to clockwork and indexes. It is to be noted that the indexes apparently read one-tenth of the actual volume passed: the index must make a complete circuit to register the amount stamped on the dial. A small index and dial are usually present for testing the meter, and a tolerance of 2% is allowed by law. This testing is done by meter-provers, carefully calibrated gas holders kept at constant temperature and the rate determined at different speeds. The meter-provers are in their turn, calibrated by a cubic foot, standardized at the Bureau of Standards. It should be noted that all this calibration is corrected, not to standard conditions (0° C. and 760 mm.), but to the cubic foot as fixed by law—gas saturated with moisture at 60° F. and 30 inches.

**The Pitot Tube.** Fig. 113. This consists of two glass-tubes, *D*, of about  $\frac{1}{4}$  inch internal diameter, inserted in the gas stream: one is bent at right angles and is set so that it receives the impact of the gas movement; the other merely registers

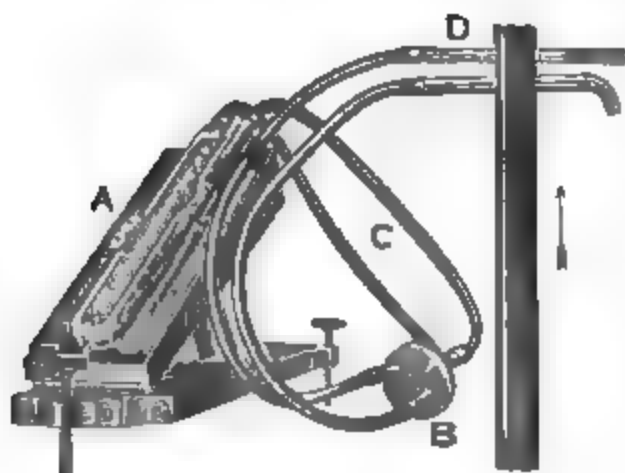


FIG. 113.

the pressure of the gas in the pipe. The point of insertion of these tubes in the chimney or duct should be in a long straight run of pipe, so as to be as free from eddies as possible. Davis<sup>1</sup> says that authorities differ as to whether the tubes should be a third or one-sixth of the diameter from the circumference to show the mean speed: he states further that each flue or chimney is a separate problem and as a result of hundreds of measurements there seems to be "no settled proportionate distance corresponding to the mean velocity."

The glass tubes are connected by rubber tubing, *C*, through a reverser, *B*, with a U-tube *A*, which is either set vertically, inclined 30°, or one in ten—this carries a vernier reading to hundredths of an inch so that readings to thousandths are feasible. The U tube is filled with solutions of different specific gravity, although ether of 0.74 sp.gr. is the one commonly employed. The difference between the arms of the U tube represents the difference between the kinetic and static pressures of the gas in the flue or chimney.

<sup>1</sup> "Handbook of Chemical Engineering," 1, 197, also for the tables for its use.

The formula for calculating the velocity recommended by W. W. Scott is

$$V = 1290 \sqrt{\frac{\frac{1}{2}h(1 + .002176t)}{BM}}$$

where  $h$  = vertical differential of gauge reading in terms of inches of water.  $\frac{1}{2}$  the reading is taken as the actual reading is double that due to flow pressure alone.  $B$  = barometric pressure of the gas in inches of mercury (29.92").  $M$  = specific gravity compared with  $H = 1$ . Air = 14.39.  $t$  = temperature of the gas.  $V$  = velocity in feet per second. The formula  $V = 42\sqrt{h}$  gives fairly accurate results. Davis formula is

$$V_0 = \sqrt{\frac{h459 + t^2}{519}} \times 28.55.$$

**The Rotameter, Fig. 114.** This is a German instrument depending upon the height to which a float is carried in a glass tube by the velocity of the stream of gas. A modification of it was used by some of the gas-lighting companies under the name of the Thorp gauge.

It consists of a graduated glass tube fixed upon a tripod and provided with a plumb line so that it can be set vertically: gas passes in at the lower end, raises the clay or talc float to a certain height and passes out at the top. The height to which the float is raised is noted on the graduations of the tube. The formula for its use is

$$V_1 = V \sqrt{\frac{M}{M_1}}$$

$V$  = volume gas as shown by reading of instrument,  $M$  its specific gravity = 1.0.

$V_1$  = volume desired,  $M_1$  = sp.gr. of gas.

It is made in all capacities from 0.2 cu.ft. per hour up.

**The Capometer. Fig. 115.** This consists of a series of capillary tubes of different sizes through which the gas is made to pass and the pressure thus produced noted in the U-tube A. Each capillary is calibrated and curves of gas flow are made corresponding to different pressures in the U-tube and various capillaries. An instrument made with capillaries 1-4 mm. in diameter has a capacity of 0.004 to 70 cu.ft. per hour.

**The Thomas Electric Gas Meter.** This depends upon the principle that if the specific heat of the gas be known, and an amount of energy be put into it, by means of a coil, sufficient to keep a certain difference



FIG. 114.

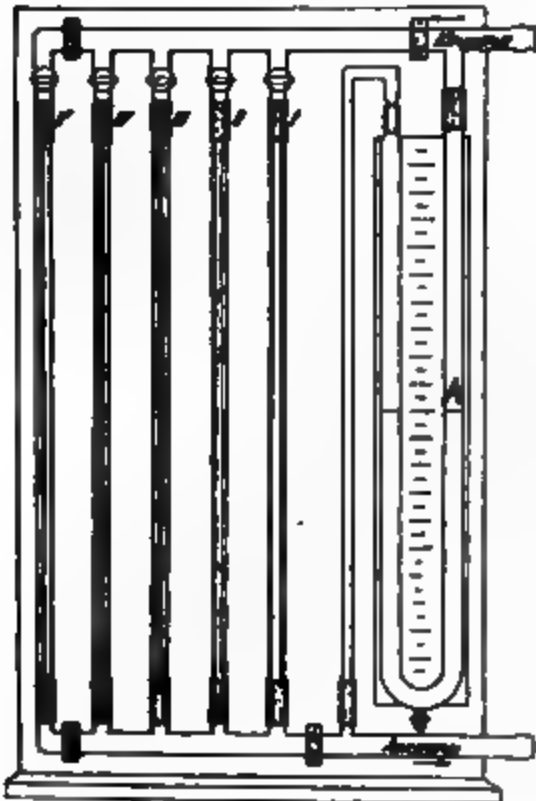


FIG. 115.

energy be put into it, by means of a coil, sufficient to keep a certain difference

of temperature between two thermometers, one before and one after the coil, this energy is a direct measure of the volume of gas flowing. Two electrical thermometers are placed in the stream of gas with a heating coil between them: 2° difference of temperature is automatically maintained between the thermometers and the energy to preserve this difference of temperature (.0127 watt hour per standard unit of gas) is read off on the meter as cubic feet of gas. It is independent of temperature or pressure changes in the gas, and is used up to gas pressures of 180 lbs. per square inch. This is used in a Western gas works measuring 200,000 ft. of gas per hour.

**The Orifice Meter.** In this the same principle is used as in measuring water, by determining the diminution in pressure as registered on delicate gauges before and after the gas has passed through a standard orifice. It is largely used for measuring natural gas.

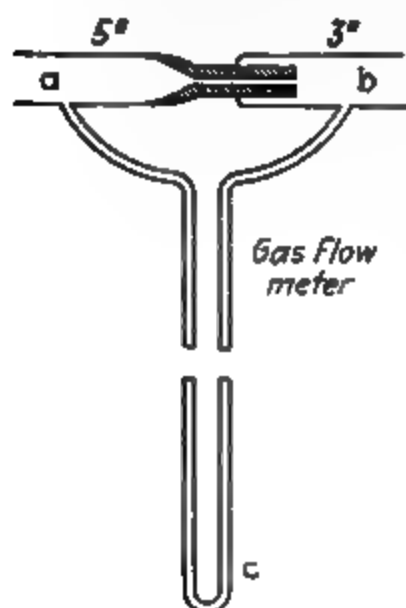


FIG 115a

**The Anemometer** is used ordinarily for measuring currents of air leaving or entering a room, analogous to its employment in meteorology.

**The Gas Flow Meter.**<sup>1</sup> This consists of a tube *a*, into which capillaries *b* of different sizes can be inserted by a rubber stopper (one at a time). On either side of the capillary is a T, the stems of which are joined together, making a U gauge *c*. This, when filled with water shows the difference in pressure of the gas before and after passing through the capillaries. The apparatus is calibrated by a wet or dry meter. It has a capacity of from 0.5 to 500 liters per hour. See Fig. 115a.

## MEASUREMENT OF GAS IN SMALL QUANTITIES. GAS BURETTES

Here may be mentioned the Hempel gas burette, made for accurate work with a compensation tube; the bulbed Orsat or Bunte burette; the separatory funnel and graduate.

**The Hempel Gas Burette,** Fig. 122, consists of a 100-cc. burette graduated in fifths of a cubic centimeter, provided with a short capillary at the top and closed with a rubber connector and pinch-cock, and a wider tube at the bottom, over which the  $\frac{3}{16}$ -in. rubber tube is drawn, which connects it with the leveling tube of similar size and length to the burette. It is manipulated by filling the leveling tube completely with water, opening the pinch-cock on the top of the burette and filling it with water. The gas to be analyzed is sucked in and measured as with the Orsat apparatus, p. 1241.

**Separatory Funnel and Graduate,** Fig. 130. From the water which has flowed out, the quantity of gas can be determined. See p. 1265.

<sup>1</sup> Benton J I & Eng Chem, 11, 623 (1919).

## ABSORPTION APPARATUS, TUBES, AND PIPETTES

These are quite varied according to the purpose for which they are intended. A very efficient form is the Friedrichs Spiral Gas Washing bottle, Fig. 116; here the gas has to pass through a long spiral path. Dennis<sup>1</sup> recommends this for the absorption of sulphur dioxide. The gas is run through a solution until a color change takes place. Were the reagent to be washed out and titrated it would not seem so well adapted on account of the difficulty of thoroughly washing it.

The Varrentrapp and Will bulbs, Fig. 117, the use of which is evident from the figure, are used for the absorption of ammonia in illuminating gas. The Wolff



Fig. 116.



Fig. 117.

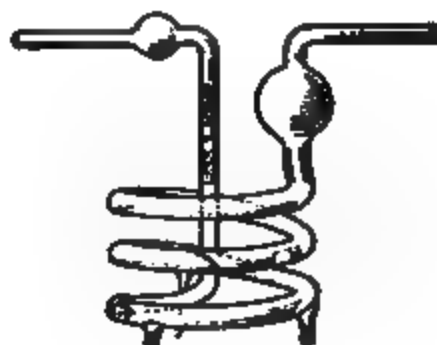


Fig. 119.



Fig. 118.

absorption tube, Fig. 118, the empty arm of which is filled with beads or broken glass is used for the absorption of carbon monoxide by blood. The bulbed tube, provided with a small jet, is generally used for containing standard solutions of acid, alkali, or potassium permanganate or, in general, a solution which is to be titrated after absorption. Where the presence of a gas as, for example, water vapor, is to be determined by the increase of weight of the reagent used, Winkler's spiral, Fig. 119<sup>2</sup>, may be employed.

**Pipettes**—Particularly for the Orsat Apparatus. These are ordinarily filled with glass tubes, but various modifications have been proposed: these are the bubbling type of Hankus, the spiral bubbling variety of Nowicki-Heinz and a combination of the Friedrichs wash bottle proposed by Dennis. All these suffer from the very serious disadvantage of a glass three-way stopcock at the top, which it is practically impossible to prevent from sticking, unless the apparatus be used by one person and that one exceptionally careful and painstaking. Dennis<sup>3</sup> has shown that one variety is no more rapid than the original and some of the others but little more so. When it is further considered that they cost four times as much,<sup>4</sup> their use would seem of doubtful expediency.

<sup>1</sup> "Gas Analysis," p. 274, 1913.

<sup>2</sup> Called "Winkler's Bulbs" in the apparatus catalogs.

<sup>3</sup> Ibid., p. 83.

<sup>4</sup> Ten dollars.

It is interesting to note further that Anderson <sup>1</sup> has shown that with the modified potassium pyrogallate which he uses, the original Orsat slightly modified, to allow the precipitate to settle, is the best.

### EXAMINATION OF THE GASES

The qualitative examination of a gaseous mixture is rarely resorted to in technical work: a sufficiently close idea of the gases present can be obtained by a consideration of the reactions involved in the various operations. It is, however, not safe to rely upon this in matters of importance, as conditions may change: for example if the gases be dry or dilute, hydrogen sulphide and sulphurous anhydride can exist together. Similarly in sewage gases, all the gas absorbed by cuprous chloride is probably not carbon monoxide. The means of identifying the different gases will be found under each gas.

#### Detection and Determination of the Various Gases

Clemens Winkler divided the gases into seven groups according to their behavior with various solvents. These were contained in suitable absorption tubes or vessels and the gases passed through them. His scheme was as follows

Gases absorbed by

- I.  $\text{H}_2\text{SO}_4$  1.7 sp.gr.;  $\text{NH}_3$ ,  $(\text{N}_2\text{O})$ ,  $\text{N}_2\text{O}_4$ .
- II.  $\text{KOH}$  1.3 sp.gr.;  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $(\text{CN})_2$ ,  $\text{HCN}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SiF}_4$ ,  $\text{CO}_2$ .
- III.  $\text{AgNO}_3$ ;  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{SbH}_3$ .
- IV. Pyro;  $\text{O}_2$ ,  $(\text{O}_3)$ .
- V.  $\text{CuCl}$ ;  $\text{CO}$ .
- VI. Acid  $\text{FeSO}_4$  1.2;  $\text{NO}$ .
- VII. Unabsorbed;  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{COS}$ , and the noble gases.

The following tables give the specific gravity referred to air, the solubility in water at  $20^\circ$ , the qualitative tests and quantitative methods of determination of these gases: additional means will be found mentioned under the several gases themselves.

GROUP I  
Gases Absorbed by  $\text{H}_2\text{SO}_4$  1.7 sp.gr.

Name.....	Ammonia.	Nitrous anhydride.	Nitrogen tetroxide.
Gravity, air = 1	0.589		1.590
Qualitative Tests....	Fumes w. $\text{HCl}$ on a rod. Nessler's reagent.	Acts like a mixture of $\text{NO}$ and $\text{NO}_2$ .	Absorb in $\text{KOH}$ , test for nitrites.
Quantitative Det'n..	Absorption in standard acid. Or $3\text{NaBrO} + 2\text{NH}_3 = \text{N}_2 + 3\text{NaBr} + 3\text{H}_2\text{O}$ . Or absorption in water and Nesslerization. pp. 291, 537.		Absorption in $\text{N}/10$ $\text{KMnO}_4$ , $2\text{KMnO}_4 + 10\text{NO}_2 + 3\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} = 10\text{HNO}_3 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4$ . Or in standard alkali.
Solubility $20^\circ\text{C}$ ., 1 cc. water absorbs cc.	678		Forms $\text{HNO}_2$ , $\text{HNO}_3$ .

<sup>1</sup> J. Ind. and Eng. Chem., 8, 131-3, 1916.

**GROUP II**  
*Gases Absorbed by KOH 1.3 sp.gr.*

Name.....	Chlorine.	Hydrochloric acid.	Cyanogen.
Gravity, air = 1.....	2.449	1.259	1.799
Qualitative Test...	KI starch paper.	Fumes w. $\text{NH}_3$ .	Pass through mixture of $\text{FeSO}_4$ 1 : 10 + $\text{KOH}$ , 1 : 3. and ppt. as Prussian blue w. ferric alum and $\text{H}_2\text{SO}_4$ . <sup>1</sup>
Quantitative Det'n..	$2\text{KI} + \text{Cl}_2 = 2\text{KCl} + \text{I}_2$ . Or absorption w. $\text{KOH}$ .	Absorption in standard alkali or silver nitrate.	
Solubility 20° C., 1 cc. water absorbs cc..	2.15	442	4.5

Hydrocyanic acid	Sulphur dioxide.	Hydrogen sulphide.	Silicon fluoride.	Carbon dioxide.
0.936	2.213	1.177	3.60	1.520
Absorption in $\text{KOH}$ and $\text{FeSO}_4$ and $\text{FeCl}_3 =$ Prussian blue. Absorption w. $\text{KOH}$ or acid $\text{AgNO}_3$ . <sup>2</sup>	Fuchsine paper bleached or $\text{KIO}_3$ starch paper. $\text{SO}_2 + 2\text{I} + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HI}$	$\text{PbAc}_2$ paper, absorption by 1 solution. $\text{H}_2\text{S} + 2\text{I} = 2\text{HI} + \text{S}$ .	None $3\text{SiF}_4 + 4\text{H}_2\text{O} = \text{SiO}_4\text{H}_4 + 2\text{H}_2\text{SiF}_6$ .	$\text{BaO}_2\text{H}_2$ on black rod. Absorption w. $\text{KOH}$ or $\text{BaO}_2\text{H}_2$ and titration.
Very sol.....	36.4	2.67	Decomposed	0.892

**GROUP III**  
*Gases Absorbed by  $\text{AgNO}_3$ .*

Name.....	Hydrogen phosphide, Phosphine.	Hydrogen arsenide, arsine.	Hydrogen antimonide, stibine.
Gravity, air = 1.....	1.175	2.696	4.330
Qualitative Test....	Neutral $\text{H}_2\text{O}$ Solution $\text{KI} + \text{HgI}_2 =$ cryst. orange yel. ppt. $\text{PHgI}_4$ . <sup>3</sup>	Blk. ppt. of $\text{AsAg}_3$ w. $\text{AgNO}_3$ .	Blk. ppt. of $\text{SbAg}_3$ w. $\text{AgNO}_3$ .
Quantitative Det'n..	Pass through $\text{Br}$ water and ppt. $\text{H}_3\text{PO}_4$ as usual.	Absorb w. $\text{NaClO}$ cont. 3% $\text{Cl}$ . <sup>4</sup>	Decompose w. tartaric acid and det. $\text{Sb}$ .
Solubility 20° C., 1 cc. water absorbs cc...	0.02	about 5	Slight.

<sup>1</sup> Nausa, J. Gasbeleuchtung, 43, 969, 1900.<sup>2</sup> Rhodes, J. Ind. and Eng. Ch., 4, 652, 1912.<sup>3</sup> Lemoult, Compt. rend, 139, 478, 1904.<sup>4</sup> Reckleben, Z. ang. Ch., 19, 275, 1906.

GROUP IV		GROUP V		GROUP VI
<i>Absorbed by potassium pyro-gallate</i>			<i>Absorbed by cuprous chloride</i>	<i>Absorbed by <math>\text{FeSO}_4</math> 1 : 2 acidulated w. <math>\text{H}_2\text{SO}_4</math></i>
Name.....	Oxygen.	Ozone.	Carbon monoxide.	Nitric oxide.
Gravity, air = 1	1.105	1.62	0.967	1.038
Qualitative Test.....	Darkening of light brown "pyro."	$\text{MnCl}_2$ paper; KI Starch paper, $\text{N}_2\text{O}_4$ and $\text{H}_2\text{O}_2$ being removed by $\text{KMnO}_4$ .	Absorb in blood, and examine w. spectroscope.	Oxidize, absorb in $\text{KOH}$ and test for nitrites.
Quantitative Det'n.....	By "Pyro." $\text{CuCl}$ in absence of $\text{CO}$		Absorption w. $\text{CuCl}$ .	Absorb in $\text{FeSO}_4$ 1 : 2 acidulated w. $\text{H}_2\text{SO}_4$ or with $\text{KMnO}_4$ as $\text{N}_2\text{O}_4$ .
Solubility $20^\circ \text{C}$ ., 1 cc. water absorbs cc.....	0.028	0.6 at $0^\circ$	0.023	0.267

GROUP VII  
Unabsorbed

Name.....	Hydrogen	Methane	Ethylene (ethene).	Acetylene (ethine).
Gravity, air = 1...	.0696	0.554	0.968	0.899
Qualitative Test..	None.	None.		Red ppt. w. am. $\text{CuCl}$ (explosive!).
Quantitative Det'n	By combustion or explosion w. $\text{O}_2$ .	By combustion or explosion w. $\text{O}_2$ .	Absorption w. $\text{Br}$ water or $\text{H}_2\text{S}_2\text{O}_7$	As $\text{C}_2\text{H}_4$ , which see.
Solubility $20^\circ \text{C}$ ., 1 cc. water absorbs cc. ...	0.0182	0.035	0.15	1.03
Nitrous oxide.	Carbon oxysulphide.	Nitrogen.	The noble gases.	
1.523	2.074	0.970	Helium, Neon, Argon, Krypton, Xenon.	
None. By explosion with $\text{H}_2$ or combustion w. $\text{CuO}$ .	None. Alcoholic $\text{KOH}$ 1 : 3 in 66% alcohol by weight.	None. By absorption or combustion of all other gases and measuring the residue which also contains the noble gases.		
0.670	0.3	0.014		

**NOTES.** GROUP I: NaBrO is made by saturating a 10% solution of caustic soda with bromine.

GROUP II: Chlorine can be removed from hydrochloric acid by passing the gas over finely powdered antimony; hydrochloric acid can be removed from chlorine by means of manganese dioxide or zinc oxide.

The following reactions will serve to discriminate between HCN and (CN)<sub>2</sub>:



Cyanogen is not absorbed by acid silver nitrate solution, from which it can be separated by drawing air through it: hydrocyanic acid is precipitated under these conditions.

GROUP IV: Ozone can be determined by Wurster's<sup>1</sup> method, consisting in passing the gas over paper moistened with fresh para phenylene diamine<sup>2</sup> and comparing the depth of color produced with a standard paper. In large quantities it can be determined according to Treadwell and Anneler<sup>3</sup> by passing through standard neutral potassium iodide and titration of the liberated iodine with N/10 sodium thiosulphate.

### Analysis of Gaseous Mixtures

The analysis of a gaseous mixture is effected by absorbing the various constituents and observing the diminution in volume: in case the gas be unabsorbable, as for example methane (CH<sub>4</sub>), it is burned and the carbon dioxide and water determined.

(a) *Analysis of mixtures for carbon dioxide, oxygen and carbon monoxide* e.g. chimney gases, producer and blast furnace gas) can be done with any of the apparatus to be described. The Orsat, or Elliott are the forms usually employed.

(b) *Analysis of mixtures as in (a) and also containing combustible gases as hydrogen and methane, e.g., illuminating gas.*

**The Orsat Apparatus. Description.** The apparatus, Fig. 120, is enclosed in a case to permit of transportation from place to place; furthermore, the measuring-tube is jacketed with water to prevent changes of temperature affecting the gas-volume. The apparatus consists essentially of the leveling-bottle A, the burette B, the

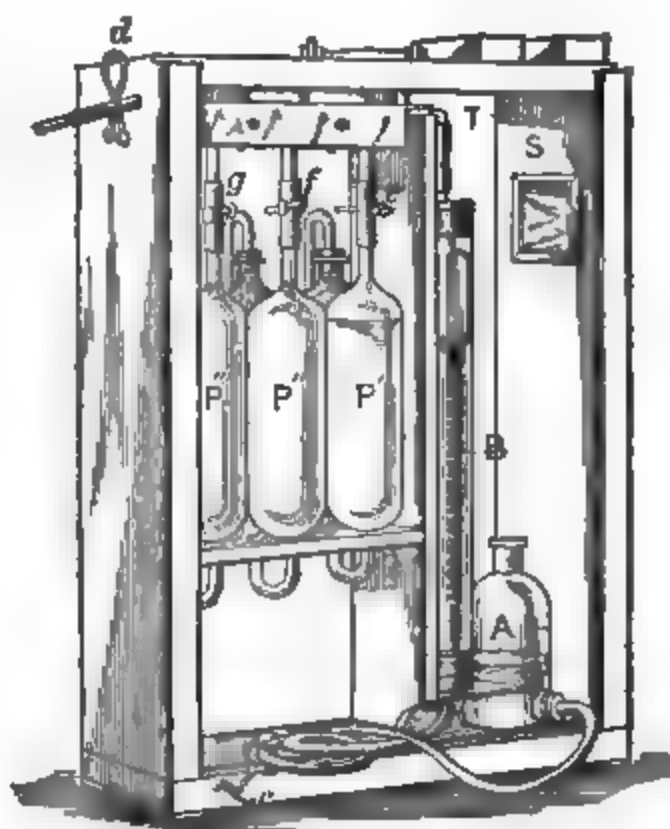


FIG. 120.

pipettes P', P'', P''', and the connecting tube T. Pipette P' is filled with potassium (or sodium) hydroxide solution (see Reagents) so that when it is drawn up into the front arm about half an inch in depth is left in the rear arm. Pipettes P'' and P''' are similarly filled with potassium (or sodium) pyrogallate and cuprous chloride solutions respectively. These reagents require to be pro-

<sup>1</sup> Berichte, 20, 921 (1888).

<sup>2</sup> Obtainable from Schuchardt, Görlitz.

<sup>3</sup> Treadwell-Hall, "Quantitative Analysis."



tected from the oxygen of the air by collapsible rubber bags. As the oxygen in the air over the reagent is absorbed, a diminution in pressure takes place rendering it difficult to bring the reagent to the point on the stem: the obvious remedy is to remove the bag temporarily and adjust the reagent. When the apparatus is first set up, one or two blank analyses should be made, to saturate the water and reagents with the gases. For example the potassium hydroxide absorbs carbon dioxide, it also absorbs about 3 cc. of oxygen, 2 cc. of carbon monoxide and 1.5 cc. of nitrogen, by virtue of the 100 cc. of water which it contains. A change of temperature of  $1^{\circ}$  makes a change of 0.36% of the volume of the gas: a change of pressure of 1 mm. produces 0.13% change in the volume.

**Manipulation.** The reagents in the pipettes should be adjusted in the capillary tubes to a point on the stem about midway between the top of the pipette and the rubber connector. This is effected by opening wide the pinchcock upon the connector, the bottle being on the table, and very gradually lowering the bottle until the reagent is brought to the point above indicated. Six inches of the tubing used correspond to but 0.1 cc., so that an error of half an inch in adjustment of the reagent is without influence upon the accuracy of the result. The reagents having been thus adjusted, the burette and connecting tube are completely filled with water by opening *d* and raising the leveling-bottle. The apparatus is now ready to receive a sample of gas (or air for practice). In case a flue-gas is to be analyzed *d* is connected with *i*, Fig. 112, *A* lowered and about 102 cc. of the gas forced over by opening *h*; or *d* may be connected with a T-joint in the gas-stream; the burette after filling is allowed to drain one minute by the sand-glass, *c* snapped upon its rubber tube, and the bottle *A* raised to the top of the apparatus. By gradually opening *c* the water is allowed to run into the burette until the lower meniscus stands upon the 100 or 0 mark (according to the graduation of the apparatus). The gas taken is thus compressed into the space occupied by 100 cc., and by opening *d* the excess escapes. Open *c* and bring the level of the water in the bottle to the same level as the water in the burette and take the reading, which should be 100 cc. Special attention is called to this method of reading: if the bottle be raised, the gas is compressed; if lowered, it is expanded.

**Determination of Carbon Dioxide.** The gas to be analyzed is invariably passed first into pipette *P'*, containing potassium hydroxide for the absorption of carbon dioxide, by opening *e* and raising *A*. The gas displaces the reagent in the front part of the pipette, laying bare the tubes contained in it, which being covered with the reagent present a large absorptive surface to the gas; the reagent moves into the rear arm of the pipette, displacing the air over it into the flexible rubber bag which prevents its diffusion into the air. The gas is forced in and out of the pipette by raising and lowering *A*, the reagent finally brought approximately to its initial point on the stem of the pipette, the burette allowed to drain one minute, and the reading taken. The difference between this and the initial reading represents the cubic centimeters of carbon dioxide present in the gas. To be certain that all the carbon dioxide is removed, the gas should be passed a second time into *P'* and the reading taken as before; these readings should agree within 0.1%.

**Determination of Oxygen.** The residue from the absorption of carbon dioxide is passed into the second pipette, *P''*, containing an alkaline solution of potassium pyrogallate, until no further absorption will take place. The difference between the reading obtained and that after the absorption of carbon dioxide, represents the number of cubic centimeters of oxygen present.

**Determination of Carbon Monoxide.** The residue from the absorption of oxygen is passed into the third pipette,  $P'''$ , containing cuprous chloride, until no further absorption takes place; that is, in this case until readings agreeing exactly (not merely to 0.1) are obtained. The difference between the reading thus obtained and that after the absorption of oxygen, represents the number of cubic centimeters of carbonic oxide present.

**Determination of Hydrocarbons.** The residue left after all absorptions have been made may consist, in addition to nitrogen, the principal constituent, of hydrocarbons and hydrogen.

**Accuracy.** The apparatus gives results accurate to 0.2 of 1%, hence figures obtained by division to 0.01 should not be reported.

**Time Required.** About twenty minutes are required for an analysis; two may be made in twenty-five minutes, using two apparatus.

**NOTES.** The method of adjusting the reagents is the only one which has been found satisfactory: if the bottle be placed at a lower level and an attempt made to shut the pinchcock  $c$  upon the connector at the proper time, it will almost invariably result in failure.

The process of obtaining 100 cc. of gas is exactly analogous to filling a measure heaping full of grain and striking off the excess with a straightedge; it saves arithmetical work, as cubic centimeters read off represent per cent directly.

It often happens when  $e$  is opened,  $c$  being closed, that the reagent  $P'$  drops, due not to a leak, as is usually supposed, but to the weight of the column of the reagent expanding the gas.

The object of the rubber bags is to prevent the access of air to the reagents, those in  $P''$  and  $P'''$  absorbing oxygen with great avidity, and hence if freely exposed to the air would soon become useless.

Carbon dioxide is always the first gas to be removed from a gaseous mixture. In the case of air the percentage present is so small, 0.08 to 0.1, as scarcely to be seen with this apparatus. It is important to use the reagents in the order given; if by mistake the gas be passed into the second pipette, it will absorb not only oxygen, for which it is intended, but also carbon dioxide; similarly if the gas be passed into the third pipette, it will absorb not only carbonic oxide, but also oxygen as well.

The use of pinchcocks and rubber tubes, original with the author, although recommended by Naef, is considered by Fischer to be inaccurate. The experience of the author, however, does not support this assertion, as they have been found to be fully as accurate as glass stopcocks, and very much less troublesome and expensive.

In case any potassium hydroxide or pyrogallate be sucked over into the tube  $T$  or water in  $A$ , the analysis is not spoiled, but may be proceeded with by connecting on water at  $d$ , opening this cock, and allowing the water to wash the tubes out thoroughly. The addition of a little hydrochloric acid to the water in the bottle  $A$  will neutralize the hydroxide or pyrogallate, and the washing may be postponed until convenient.

After each analysis the number of cubic centimeters of oxygen and carbonic oxide should be set down upon the ground-glass slip provided for the purpose. By adding these numbers and subtracting their sum from the absorption capacity (see Reagents) of each reagent, the condition of the apparatus is known at any time, and the reagent can be renewed in season to prevent incorrect analyses.

**Elliott Apparatus. Description.** The apparatus Fig. 121 consists of a burette holding 100 cc. graduated in tenths of a cubic centimeter and bulbed like the Bunte apparatus—the bulb holding about 30 cc.; it is connected with a leveling-bottle similar to the Orsat apparatus. The top of the burette ends in a capillary stopcock, the stem of which is ground square to admit of close connection with the “laboratory vessel,” an ungraduated tube similar to the burette, except of 125 cc. capacity.

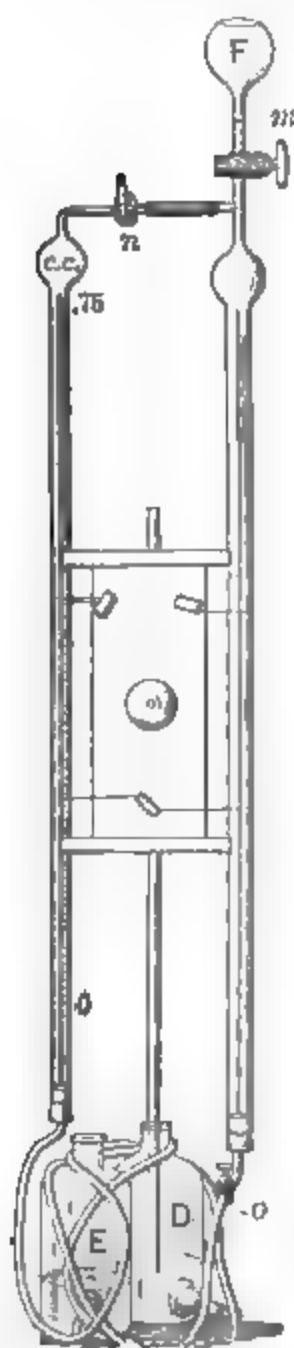


FIG. 121.

The top of this “vessel” is also closed with a capillary stopcock, carrying by a ground-glass joint, or better a rubber stopper, a thistle-tube *F*, for the introduction of the reagents. The lower end of this “vessel” is closed by a rubber stopper carrying a three-way cock *o*, and connected with a leveling bottle *D*. The burette and vessel are held upon a block of wood—supported by a ring stand—by fine copper wire tightened by violin keys.

**Manipulation.** The ground-glass joints are lubricated with stopcock grease, p.1269. The leveling-bottles are filled with water, the stopcocks opened, and the bottles raised until the water flows through the stopcocks *m* and *n*. *m* is connected with the source whence the gas to be analyzed is to be taken, *n* is closed, *D* lowered and rather more than 100 cc. drawn in, and *m* closed. *n* is opened, *D* raised and *E* lowered, nearly 100 cc. of gas introduced, and *n* closed; by opening *m* and raising *D* the remainder of the gas is allowed to escape, the tubes being filled with water and *m* closed. *n* is opened and the water brought to the reference mark; the burette is allowed to drain one minute, the level of the water in *E* is brought to the same level as in the burette, and the reading taken.

**Determination of Carbon Dioxide.** By raising *E*, opening *n*, and lowering *D*, the gas is passed over into the laboratory vessel; *F* is filled within half an inch of the top with potassium hydroxide, *o* closed, *m* opened, and the reagent allowed slowly to trickle in. A No. 3 evaporating dish is placed under *o*, and this turned to allow the liquid in the laboratory vessel to run into the dish. At first this is mainly water, and may be thrown away; later it becomes diluted reagent and may be returned to the thistle-tube. When the depth of the reagent in the thistle-tube has lowered to half an inch, it should be refilled either with fresh or the diluted reagent and allowed to run in until the absorption is judged to be complete, and the gas passed back into the burette for measurement. To this end close *o* and then *m*, raise *E*, open *n*, and force some pure water into the laboratory vessel, thus rinsing out the capillary tube. Now raise *D* and lower *E*, shutting *n* when the liquid has arrived at the reference-mark. The burette is allowed to drain a minute, the level of the water in the bottle *E* brought to the same level as the water in the burette, and the reading taken.

**Determination of Oxygen.** The manipulation is the same as in the preceding determination, potassium pyrogallate being substituted for potassium hydrate; the apparatus requiring no washing out.

**Determination of Carbonic Oxide.** The laboratory vessel, thistle-tube, and bottle if necessary, are washed free from potassium pyrogallate and the absorption made with acid cuprous chloride similarly to the determination of carbon dioxide. The white precipitate of cuprous chloride may be dissolved by hydrochloric acid.

**Accuracy and Time Required.** The apparatus is as accurate for absorptions as that of Orsat; it is stated to be much more rapid—a claim which the writer cannot substantiate. It is not as portable, is more fragile, and more troublesome to manipulate, and as the burette is not jacketed, it is liable to be affected by changes of temperature.

**NOTES.** In case at any time it is desired to stop the influx of reagent, *o* should be closed first and then *m*; the reason being that the absorption may be so rapid as to suck air in through *o*, *m* being closed.

The stopcock should be so adjusted as to cause the reagent to spread itself as completely as possible over the sides of the burette.

By the addition of an explosion tube it is used for the analysis of illuminating gas,<sup>1</sup> bromine being used to absorb the "illuminants." Winkler<sup>2</sup> states that this absorption is incomplete; later work by Treadwell and Stokes, and also Korhuly,<sup>3</sup> has shown that bromine water, by a purely physical solution, does absorb the "illuminants" completely; Hempel<sup>4</sup> states that explosions of hydrocarbons made over water are inaccurate, so that the apparatus can be depended upon to give results upon methane and hydrogen only within about 2%. It is, however, very rapid, a complete analysis of illuminating gas can be made with it in fifty-five minutes.

**Hempel's Apparatus. Description.** The apparatus, Figs. 122 and 123, is very similar in principle to that of Orsat; the burette is longer, admitting of the reading of small quantities of gas, and the pipettes are separate and mounted in brass clamps on iron stands. *P* shows a "simple" pipette<sup>5</sup> provided with a rubber bag; this form, after twenty-five years of use, can be said satisfactorily to take the place of the cumbersome "compound" pipette.

The pipette for fuming sulphuric acid<sup>6</sup> is shown at *F*, and differs from the ordinary in that vertical tubes after the manner of those in the Orsat pipettes replace the usual glass beads. This prevents the trapping of any gas by the filling, which was so common with the beads and glass wool. *E* represents the large explosion pipette,<sup>7</sup> of about 250-cc. capacity, with walls half an inch thick; the explosion wires enter at the top and bottom to prevent short-circuiting; mercury is the confining liquid. The small explosion pipette holds about 110 cc. and is of glass, the same thickness as the simple pipettes. Water is here used as the confining liquid, and also usually in the burette.

An induction coil capable of giving a half-inch spark, with six dry cells, four "simple" pipettes and a mercury burette, complete the outfit.

The burette should be carefully calibrated and the corrections may very well be etched upon it opposite the 10-cc. divisions.

In working with the apparatus the pipettes are placed upon the adjustable stand *S* and connection made with the doubly bent capillary tube.

**Manipulation.** To acquire facility with the use of the apparatus before proceeding to the analysis of illuminating gas, it is well to make the following

<sup>1</sup> Mackintosh, *Am. Chem. Jour.*, 9, 294.

<sup>2</sup> *Zeit. f. Anal. Chem.*, 28, 286.

<sup>3</sup> Treadwell-Hall's "Quantitative Analysis" p. 569.

<sup>4</sup> "Gasanalytische Methoden," p. 102.

<sup>5</sup> Gill, *Am. Chem. J.*, 14, 231, 1892.

<sup>6</sup> *Ibid.*, *J. Am. Chem. Soc.*, 18, 67, 1896.

<sup>7</sup> Gill, *J. Am. Chem. Soc.*, 17, 771, 1895.

determinations, obtaining "check-readings" in every case: I. Oxygen in air, by (1) absorption with phosphorus; (2) absorption with potassium (or sodium) pyrogallate;<sup>1</sup> (3) by explosion with hydrogen.

### I. DETERMINATION OF OXYGEN IN AIR

(1) **By Phosphorus.** 100 cc. of air are measured out as with the Orsat apparatus, the burette being allowed to drain two minutes. The rubber connectors upon the burette and pipette are filled with water, the capillary tube inserted, as far as it will go, by a twisting motion, into the connector upon the burette, thus filling the capillary with water; the free end of the capillary is inserted into the

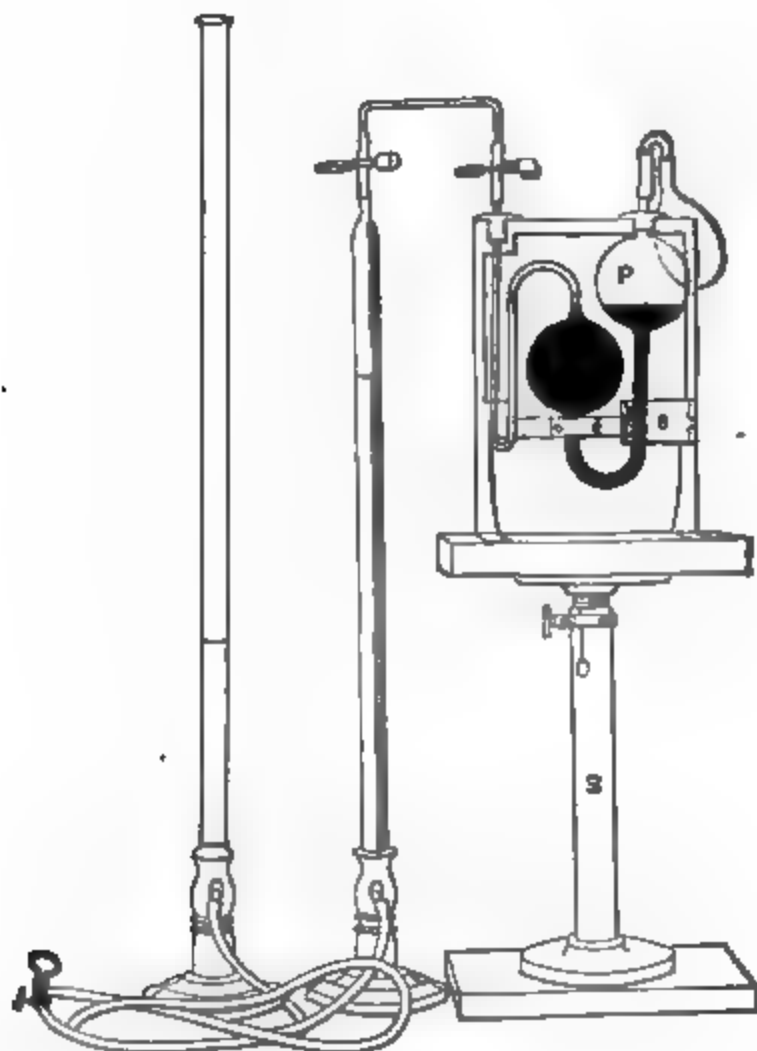


FIG. 122.

pipette connector, the latter pinched so as to form a channel for the water contained in it to escape, and the capillary twisted and forced down to the pinchcock. There should be as little free space as possible between the capillaries and the pinchcock. Before using a pipette, its connector (and rubber bag) should be carefully examined for leaks, especially in the former, and if any found the faulty piece replaced.

The pinchcock on the burette and pipette are now opened, the air forced over into the phosphorus, and the pinchcock on the pipette closed; action immediately

<sup>1</sup> The writer finds after an experience of more than twenty-five years in the laboratory with hundreds of students, that sodium pyrogallate can be used with practically the same results as the potassium compound. The absorption is complete, as shown by subsequent treatment with cuprous chloride.

ensues, shown by the white fumes; after allowing it to stand fifteen minutes the residue is drawn back into the burette, the latter allowed to drain and the reading taken. The absorption goes on best at 20° C., not at all below 15° C.; it is very much retarded by small amounts of ethane and ammonia. It cannot be used to absorb commercial oxygen. No cognizance need be taken of the fog of oxides of phosphorus.

(2) **By Pyrogallate of Potassium.** 100 cc. of air<sup>1</sup> are measured out as before, the carbon dioxide absorbed with potassium hydrate and the oxygen with potassium pyrogallate, as with the Orsat apparatus; before setting aside the pyrogallate pipette, the number of cubic centimeters of oxygen absorbed should be noted upon the slate *s* on the stand. This must never be omitted with any pipette save pos-

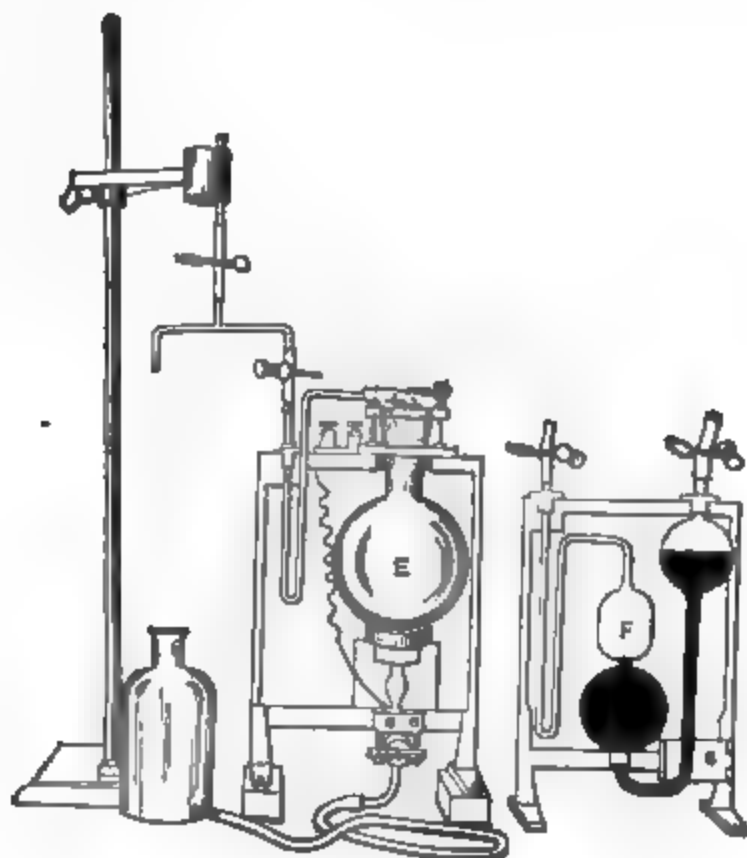


FIG. 123.

sibly that for potassium hydroxide, as failure to do this may result in the ruin of an important analysis. The reason for the omission in this case is found in the large absorption capacity—four to five liters of carbon dioxide—of the reagent.

(3) **By Explosion with Hydrogen.** Forty-three cc. of air and 57 cc. of hydrogen are measured out, passed into the small explosion pipette, the capillary of the pipette filled with water, the pinchcocks and glass stopcock all closed, a heavy glass or fine wire gauze screen placed between the pipette and the operator, the spark passed between the spark wires, and the contraction in volume noted. *The screen should never be omitted, as serious accidents may occur thereby.* The oxygen is represented by one-third of the contraction. For very accurate work the sum of the combustible gases should be but one-sixth that of the non-combustible gases, otherwise some nitrogen will burn and high results will be obtained;<sup>2</sup> that is,  $(H+O) : (N+H) :: 1 : 6$ .

<sup>1</sup>See Anderson's work, *J. Ind. and Chem.*, 7, 587, 1915.

<sup>2</sup>This is shown in the work of Gill and Hunt, *J. Am. Chem. Soc.*, 17, 987, 1895.

## II. ANALYSIS OF ILLUMINATING GAS

One hundred cc. of gas are measured from the bottle containing the sample into the burette.

**Determination of Carbon Dioxide.** The burette is connected with the pipette containing potassium hydroxide and the gas passed into it with shaking until no further diminution in volume takes place.

**Illuminants,  $C_nH_m$ ,  $C_nH_{m-4}$  Series.**—The rubber connectors are carefully dried out with filter-paper, a dry capillary used, and the gas passed into the pipette containing fuming sulphuric acid and allowed to stand, with occasional passes to and fro, for forty-five minutes. On account of the extremely corrosive nature of the absorbent it is not advisable to shake the pipette, as in case of breakage a serious accident might occur. For water gas this is sufficient, although in case of doubt or with richer gases check readings to 0.2 cc. should be obtained. It is then passed into potassium hydroxide, as in the previous determination, to remove any sulphurous acid which may have been formed and any sulphuric anhydride vapor, these having a higher vapor tension than water. The difference between this last reading and that after the absorption of the carbon dioxide represents the volume of "illuminants" or "heavy hydrocarbons" present.

As has already been stated, page 1245, saturated bromine water may replace the fuming sulphuric acid. Fuming nitric acid is not recommended, as it is liable to oxidize carbonic oxide.

**Oxygen.** This is absorbed, as in the analysis of air, by potassium or sodium pyrogallate.

**Carbonic Oxide.** The gas is now passed into ammoniacal cuprous chloride, until the reading is constant to 0.2 cc.; it is then passed into a second pipette, which is fresh, and absorption continued until constant readings are obtained. The second pipette should not have absorbed more than 10 cc. of CO.

Gautier and Clausmann<sup>1</sup> have shown that some carbonic oxide escapes solution in cuprous chloride, so that for very accurate work it may be necessary to pass the gas through a U-tube containing iodic anhydride heated to 70° C.

This is done by interposing this tube between the burette and a simple pipette filled with potassium hydrate. The reaction is  $5CO + I_2O_5 = 5CO_2 + 2I$ . The diminution in volume represents directly the volume of carbonic oxide present.

The volume of air contained in the tube should be corrected for as follows: One end of the tube is plugged tightly and the other end connected with the gas burette partly filled with air. A bath of water at 9° C. is placed around the U-tube and the reading of the air in the gas burette recorded when constant; the bath is now heated to 100° and the burette reading again recorded when constant. The increase in reading represents one-third the volume of the U-tube,  $273 : 273 + (100 - 9) :: 3 : 4$ .

**Methane and Hydrogen.** (a) *Hinman's Method.*<sup>2</sup> The gas left from the absorption of carbonic oxide is passed into the large explosion pipette. About half the requisite quantity of oxygen (40 cc.) necessary to burn the gas is now added, mercury introduced through the T in the connector sufficient to seal the capillary of the explosion pipette, all rubber connectors carefully wired, the pinch-cocks closed, and the pipette cautiously shaken. A screen of heavy glass or fine wire gauze is interposed between the operator and the apparatus, the explosion

<sup>1</sup> Bull. Soc. Chem., 25, 513; Abstr. Analyst, 31, 349, 1906.

<sup>2</sup> Gill and Hunt, J. Am. Chem. Soc., 17, 987, 1895.

wires are connected with the induction coil, a spark passed between them and the pinchcocks opened, sucking in the remainder of the oxygen. The capillary is again sealed with mercury, the stopcock opened and closed, to bring the contents of the pipette to atmospheric pressure, and the explosion repeated as before, and the stopcock opened.

It may be found expedient to increase the inflammability of the mixture, to introduce 5 cc. of "detonating gas," the hydrolytic mixture of hydrogen and oxygen. The gas in the pipette containing carbon dioxide, oxygen, and nitrogen is transferred to the mercury burette and accurately measured. The carbon dioxide resulting from the combustion of the marsh gas is determined by absorption in potassium hydroxide; to show the presence of an excess of oxygen, the amount remaining is determined by absorption with potassium pyrogallate.

The calculation is given on page 1250. For very accurate work a second analysis should be made, making successive explosions, using the percentages of methane and hydrogen just found as a basis upon which to calculate the quantity of oxygen to be added each time. The explosive mixture should be so proportioned that the ratio of combustible gas (i.e.,  $\text{CH}_4$ , H and O) is to the gases which do not burn (i.e., N and the excess of  $\text{CH}_4$  and H) as 100 is to about 50 (from 26 to 64);<sup>1</sup> otherwise the heat developed is so great as to produce oxides of nitrogen, which, being absorbed in the potassium hydroxide, would affect the determination of both the methane and the hydrogen. The oxygen should preferably be pure, although commercial oxygen, the purity of which is known, can be used; the oxygen content of the latter should be tested from time to time, especially with different samples.

(b) *Hempel's Method.*<sup>2</sup> From 12 to 15 cc. of the gas are measured off into the burette (e.g., 13.2 cc.) and the residue is passed into the cuprous chloride pipette for safe keeping. That in the burette is now passed into the small explosion pipette; a volume of air more than sufficient to burn the gas, usually about 85 cc., is accurately measured and also passed into the explosion pipette, and in so doing water from the burette is allowed partially to fill the capillary of the pipette and act as a seal. The rubber connectors upon the capillaries of the burette and pipette are carefully wired on, both pinchcocks shut, and the stopcock closed. The pipette is cautiously shaken, the screen interposed, the explosion wires connected with the induction coil, a spark passed between them, and the stopcock immediately opened. The gas in the pipette, containing carbon dioxide, oxygen, and nitrogen, is transferred to the burette, accurately measured, by reading immediately, to prevent the absorption of carbon dioxide, and carbon dioxide and oxygen determined in the usual way.

**Calculation.** (a) *Hinman's Method.* 56.2 cc. of gas remained after the absorption; 77.4 cc. of oxygen were introduced, giving a total volume of 133.6 cc.

Residue after explosion.....	46.9 cc.
Residue after $\text{CO}_2$ absorption .....	28.2
Carbon dioxide formed.....	18.7
Contraction.....	$133.6 - 46.9 = 86.7$
Residue after O absorption .....	25.6
Oxygen in excess.....	$28.2 - 25.6 = 2.6$

<sup>1</sup> Bunsen, "Gasometrische Methoden," 2d ed., 73, 1877.

<sup>2</sup> Hempel, "Gas Analytische Methoden," 3d ed., 245, 1901.



The explosion of marsh gas or methane is represented by the equation

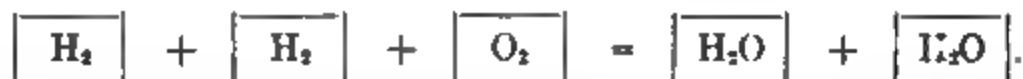


From this it is evident that the volume of carbon dioxide is equal to the volume of methane present; therefore in the above example, in the 56.2 cc. of gas burned, there were 18.7 cc. methane.

The total contraction is due (1) to the disappearance of oxygen in combining with the hydrogen of the methane, and (2) to the union of the free hydrogen with oxygen. The volume of the methane having been found, (1) can be ascertained from the equation above, equals twice the volume of the methane; hence

$$86.7 - (2 \times 18.7) = 49.3 \text{ cc.},$$

contraction which is due to the combustion of hydrogen. This takes place according to the following reaction:<sup>1</sup>



Hydrogen then requires for its combustion half its volume of oxygen, hence this 49.3 cc. represents a volume of hydrogen with  $\frac{1}{2}$  its volume of oxygen, or  $\frac{3}{4}$  volumes; hence the volume of hydrogen is 32.9 cc.

(b) *Hempel's Method.* Of the 82 cc. of gas remaining after the absorptions, 13.2 cc. were used for the explosion; 86.4 cc. air introduced, giving a total volume of 99.6 cc.

Residue after explosion.....	78.0 cc.
Residue after CO <sub>2</sub> absorption.....	73.2
Carbon dioxide formed.....	4.8
Contraction.....	99.6 - 78.0 = 21.6
Residue after O absorption.....	70.2
Oxygen in excess.....	73.2 - 70.2 = 3.0

The carbon dioxide being equal to the methane present, in the 13.2 cc. of gas burned there were 4.8 cc. of methane. The volume of methane is found by the proportion  $13.2 : 82 :: 4.8 : x$ , whence  $x = 29.8$  cc.

The hydrogen is calculated similarly.

Another method for the estimation of hydrogen is by absorption with palladium sponge;<sup>2</sup> it, however, must be carefully prepared, and it is the author's experience that one cannot be sure of its efficacy when it is desired to make use of it. A still better absorbent of hydrogen<sup>3</sup> is a 1% solution of palladous chloride at 50° C.; when fresh this will absorb 20-50 cc. of hydrogen in ninety minutes. A proportionately longer time is required if more hydrogen be present or the solution nearly saturated. The methane could then be determined by explosion or by mixing with air and passing to and fro over a white-hot platinum spiral in a tubulated pipette called the grisoumeter<sup>4</sup> (grisou = methane).

**Nitrogen.** There being no direct and convenient method for its estimation with this apparatus, the percentage is obtained by finding the difference between the sum of all percentages of the gases determined and 100%.

<sup>1</sup> H<sub>2</sub>O being as steam at 100° C. At ordinary temperatures this is condensed, giving rise to "total contraction"

<sup>2</sup> Hempel, *Berichte*, 12, 636 and 1006, 1879.

<sup>3</sup> Campbell and Hart, *Am. Chem. J.*, 18, 294, 1896.

<sup>4</sup> Winkler, *Fres. Zeit.*, 28, 269 and 288.

New<sup>1</sup> determined nitrogen in illuminating gas directly after the method of Dumas in organic substances; 150 cc. of gas are used, the hydrocarbons partially absorbed by fuming sulphuric acid and the remainder burned in a combustion tube with copper oxide; the carbon dioxide is absorbed and the residual nitrogen collected and measured.

**Accuracy and Time Required.** For the absorptions the apparatus is accurate to 0.1 cc.; for explosions by Hinman's method<sup>2</sup> the methane can be determined within 0.2%, the hydrogen within 0.3%; by Hempel's method within 1% for the methane and 7.5% for the hydrogen. The time required for the analysis of illuminating gas is from three to three and one-half hours; for air, from fifteen to twenty minutes.

**NOTES.** The object in filling the capillaries of the explosion pipettes with water or mercury before the explosion is to prevent the bursting of the rubber connectors on them. With mercury this is effected by introducing it through the T-joint in the connector. After testing for oxygen with the pyrogallate a small quantity of dilute acetic acid is sucked into the burette to neutralize any alkali which by any chance may have been sucked over into it. The acid is rinsed out with water and this is forced out by mercury before the burette is used again.

The water in the burette should be saturated with the gas which is to be analyzed—as illuminating gas—before beginning an analysis. The reagents in the pipettes should also be saturated with the gases for which they are not the reagent. For example, the fuming sulphuric acid should be saturated with oxygen, carbon monoxide, methane, hydrogen, and nitrogen; this is effected by making a blank analysis, using illuminating gas.

The method of analysis of the residue after the absorptions have been made by explosion is open to two objections: 1st, the danger of burning nitrogen by the violence of the explosion; and 2d, the danger of breakage of the apparatus and possible injury to the operator. These may be obviated by employing the apparatus of Dennis and Hopkins,<sup>3</sup> which is practically a grisoumeter with mercury as the confining liquid; or that of Jaeger,<sup>4</sup> who burns the gases with oxygen in a hard-glass or quartz tube filled with copper oxide. By heating to 250° C. nothing but hydrogen is burned; higher heating of the residue burns the methane. Recent work shows this procedure to be very slow and not very accurate. Or the mixture of oxygen and combustible gases, bearing in mind the ratio mentioned at the bottom of page 1247, can be passed to and fro through Drehschmidt's<sup>5</sup> capillary heated to a bright redness. This consists of a platinum tube 20 cm. long, 2 mm. thick, 1.7 mm. bore, filled with three platinum or palladium wires. The ends of the tube are soldered to capillary brass tubes and arranged so that these can be water cooled. It is inserted between the burette and a simple pipette, mercury being the confining liquid in both cases. The air contained in the tube can be determined as in the case of the tube containing iodic anhydride, page 1248.

To the method of explosion by the mixture of an aliquot part of the residue with air, method (b), there is the objection that the carbon dioxide formed is measured over water in a moist burette, giving abundant opportunities for its absorption, and that the errors in analysis are multiplied by about six, in the example by  $\frac{6}{1}$ .

<sup>1</sup> J. Soc. Chem. Ind., 11, 415, 1892.

<sup>2</sup> Gill and Hunt, loc. cit.

<sup>3</sup> J. Am. Chem. Soc., 21, 398, 1899.

<sup>4</sup> J. Gasbeleuchtung, 41, 764. Abstr. J. Soc. Chem. Ind., 17, 1190, 1898.

<sup>5</sup> Berichte, 21, 3242, 1888.

## APPLICATIONS OF GAS ANALYSIS AND INTERPRETATION OF RESULTS

It is only within comparatively recent times that Gas Analysis has assumed any importance. The reasons are that the substances with which it deals are so intangible, the apparatus is complicated and fragile, and until lately, competition has not compelled manufacturers to seek every possible source of loss.

Some of its applications are to:

- I. Chimney and flue gases;
- II. Producer and fuel gases;
- III. Illuminating gas;
- IV. Sulphuric acid gases;
- V. Mine gases;
- VI. Electrolytic gases;
- VII. Acetylene;
- VIII. Atmospheric air.

### I. CHIMNEY AND FLUE GASES

Here the object is to keep the carbonic acid ( $\text{CO}_2$ ) as high as possible, and to avoid the formation of carbon monoxide: in large plants every additional per cent of carbonic acid means the saving of tons of coal. Savings of 20 to 33% by the use of gas analysis alone, have frequently come to the writer's notice. A satisfactory procedure is to post in the fire-room the percentage of carbonic acid obtained by each stoker, and stimulate a rivalry among the men—a bonus in the pay envelope is also effective. The determinations to be made are:

**Analysis of Chimney Gases.** Determination of carbon dioxide, oxygen, carbon monoxide, nitrogen, and in some case hydrocarbons. For this purpose the Orsat apparatus is widely employed: the hydrocarbons may be determined by the Hempel apparatus.

Usually a few determinations of carbonic acid will suffice, but for regular work the installation of some form of registering carbonic acid indicator should be installed.

**Carbonic Acid Indicators.**<sup>1</sup> These usually depend upon the principle of collecting 100 cc. of the gas, causing it to pass through a suitable absorber and collecting the residue in a bell which floats to a greater or less height according to the residual volume. The fluctuations of this bell are recorded after the usual manner of self-registering barometers or thermometers: the usual time for this analysis and record is five minutes.

By modifying this apparatus slightly, it can be applied to the determination of any absorbable gas as, for example, sulphurous acid or chlorine. It has been adapted to carbon monoxide absorption, but it is not usual or easy.

Haber<sup>2</sup> employs the refractive index of gases to determine the amount of carbonic acid in chimney gas; it gives results within half of 1%;<sup>3</sup> it has also been

<sup>1</sup> These can be obtained from the following: Combustion Appliance Co., Chicago; Precision Instrument Co., Detroit; Uehling Instrument Co., Passaic. See Bureau of Mines Bulletin No. 91, "Instruments for Recording Carbon Dioxide in Flue Gases."

<sup>2</sup> Z. Ang. Chem., 19, 1418, 1906; *ibid.*, 23, 1393, 1910.

<sup>3</sup> Mohr, *ibid.*, 25, 1313, 1912.

applied to other gaseous mixtures. The instrument is called the Interferometer or Gas Refractometer and is made by Zeiss of Jena.<sup>1</sup>

**The Determination of Temperature.** This is done by inserting a thermometer, mounted in a metal tube, on the chimney side of the gas sampling tube. These resemble those used for determining steam temperatures or for "running" varnish. It should register to 360° and, under certain circumstances, one showing 550° may be desirable. A chemical thermometer with long stem may also be employed; it should never be inserted naked into the flue—as a sudden hot blast may break it—but always in a tube of cotton-seed oil or sea sand.<sup>2</sup> These thermometers should be tested for accuracy by comparison with a standard, in a carefully stirred oil bath. The standard should be kept exclusively for the purpose and be allowed to stay in the bath until cool. Sudden cooling of a thermometer changes the zero point. The standard can be certified by the makers or the United States Bureau of Standards.

Electric pyrometers are also of course available for these measurements. An error of five degrees (5°) in the reading of the thermometer affects the final result by about 20 calories.

In case none of these appliances be at hand, the maximum temperature can be determined by utilizing the melting-points of certain pure salts or metals; as tin 232°, bismuth 270°, cadmium 302°, lead 327°, zinc 419°, cadmium chloride 541°, antimony 630°, etc. These can be suspended in the chimney in small covered cast-iron boxes.

**Composition of the Coal.** This is determined by the usual methods of organic combustion and is required only for very accurate work.

**Calculation:**

- a. Heat passing up chimney;
- b. Pounds of air per pound of coal.

(a) *Heat Passing up Chimney.* The accurate calculation resolves itself into finding what volume of gas of the composition determined by analysis would be produced by a kilo of the coal used, and whose analysis is known. The temperature of the escaping chimney gases being also known, and their specific heat, the quantity of heat they carry off can be calculated: this divided by the calorific power of the coal gives the per cent of heat lost in the chimney gases. The calculation is rather long and will be found in detail in the author's book.<sup>3</sup>

The formula of Shields.<sup>4</sup>

$$\text{Per cent heat lost} = \frac{\text{Per cent carbon in coal}}{\text{Heating value of coal}} \times \frac{200 + \text{per cent CO}_2}{\text{Per cent CO}_2 + \text{per cent CO}} \times \text{rise in temperature in } ^\circ\text{C.} \times 0.2864,$$

gives results usually 0.5% low, as no cognizance has been taken of the water vapor.

Another formula<sup>5</sup> in which only the carbon dioxide and its temperature enters was proposed by Bunte and gives close results.

For every per cent of carbonic acid present 43.43 calories per cubic meter of

<sup>1</sup> Bureau of Mines Technical Paper 185, "Use of the Interferometer in Gas Analysis," 1918.

<sup>2</sup> With rounded grains, not river sand, as it would make scratches.

<sup>3</sup> "Gas and Fuel Analysis for Engineers," Wiley.

<sup>4</sup> "Power," 29, 1121, 1909.

<sup>5</sup> J. J. Gasbeleuchtung, 43, 637, 1900.

flue gases have been developed =  $W$ ;  $C$  = specific heat of the flue gases per cubic meter; then  $W/C$  represents the initial temperature (which is never attained) the ratio of which to the actual exit temperature of the flue gases shows the heat lost. If  $T$  = this initial temperature and  $t$  the rise of temperature of the flue gases, then  $t/T$  represents the heat lost in the chimney gases.

The following table gives the data for the calculation for both pure carbon and coal of average value:

Per Cent of CO <sub>2</sub> in Chimney Gas.	Specific Heat of Chimney Gas.	Initial Temperature, $W/C$ . Degrees C.		
		For Carbon = $T$ .	For Coal = $T$ .	Diff. for 0.1% CO <sub>2</sub> .
1	0.308	141	167	16
2	0.310	280	331	16
3	0.311	419	495	16
4	0.312	557	652	16
5	0.313	694	808	15
6	0.314	830	961	15
7	0.315	962	1112	15
8	0.316	1096	1261	15
9	0.318	1229	1407	14
10	0.319	1360	1550	14
11	0.320	1490	1692	14
12	0.322	1621	1830	14
13	0.323	1750	1968	13
14	0.324	1880	2102	13
15	0.324	2005	2237	13
16	0.325	2130	2366	13

If there were 11.5% carbonic acid, the initial temperature  $T$  would be 1762°; the rise of temperature in the chimney gases is 250°, the loss is  $\frac{250}{1762}$  or 14.2%. The accurate calculation gives 14.1.

Finally, for very rapid work, Bunte's Chart, Table V, may be used. The results are within 2% for about 12% of carbonic acid. It is used by noting the point where the diagonal line representing CO<sub>2</sub> cuts the ordinate of temperature—the abscissa corresponding to this point represents the per cent loss.

The following table shows roughly the excess of air, and per cent of heat lost in the chimney gases, their temperature being 518° F.

Per cent CO <sub>2</sub>	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Vol air more than theory = 10.	9.5	6.3	4.7	3.8	3.2	2.7	2.4	2.1	1.9	1.7	1.6	1.5	1.4	1.3
Per cent loss of heat. . .	90	60	45	36	30	26	23	20	18	16	15	14	13	12

If the oxygen be from 1.5% to 2% with the temperature of escaping gases 400–500° F., the fires are too thick; if it be more than 8% they are too thin.

(b) *Pounds of Air per Pound of Coal.* This can be determined by calculating the ratio of carbon to oxygen in the carbonic acid and carbon monoxide and oxygen of the chimney gases, or by the formula of Shields.<sup>1</sup>

<sup>1</sup> Loc. cit.

$$\text{Pounds of air per pound of coal} = 2.31 \frac{\text{Per cent of carbon in coal}}{\text{Per cent CO}_2 + \text{per cent CO}}$$

**Loss Due to Carbonic Oxide.** For every gram of carbon burned to carbonic oxide there is a loss of 5.66 calories.

**Smoke.** For the determination of the amount of smoke in the chimney gases, use may be made of the Ringelmann smoke scale. This consists<sup>1</sup> of a series of rectangles  $\frac{1}{8}$  in.  $\times$   $\frac{1}{8}$  in. filled with cross-hatching lines a greater or less distance apart, with which the density of the smoke can be compared. Or the Eddy smoke recorder<sup>2</sup> may be employed; this consists of a tube of standard length through which the smoke gases are drawn. A standard electric light is fixed at one end of the tube and viewed through the smoke; its density is measured by the extent to which the light is obscured.

## II. PRODUCER AND FUEL GASES. BLAST-FURNACE GAS

Here the object is the reverse of that in the chimney gases, to keep the percentage of carbon monoxide as high as possible and, for gas-engine purposes, the per cent of hydrogen constant.

The determinations made are the same as in chimney gas—CO<sub>2</sub>, O, CO,<sup>3</sup> N, and oftentimes hydrogen and hydrocarbons; the quantity of *dust* is sometimes important. The heating value is determined as in illuminating gas, p. 713. The efficiency of conversion would be found by measuring the number of cubic feet of gas made per ton of coal gasified; the calorific power of each (gas and coal) being known, their quotient represents the efficiency. The heat contained in the gas due to its sensible heat, found after the manner of calculating the loss in chimney gases (i.e., volume gas  $\times$  weight  $\times$  rise of temperature  $\times$  specific heat) is to be added to this for accurate work.

As showing producer gas practice, the following typical analyses are cited:

	Anthracite. <sup>4</sup>	Bituminous <sup>5</sup>	Blue Water Gas. <sup>6</sup>	Lignite. <sup>7</sup>	Peat. <sup>8</sup>	Tan. <sup>9, 10</sup>	Wood. <sup>11</sup>
CO .....	27.0	27.0	45.0	22.0	30.6	14.2	13.3
H <sub>2</sub> .....	12.0	12.0	45.0	9.6	6.1	8.7	21.0
CH <sub>4</sub> .....	1.2	2.5	2.0	1.6	5.1	5.6	2.6
C <sub>2</sub> H <sub>4</sub> .....	.....	0.4	.....	0.7	.....	.....	0.3
CO <sub>2</sub> .....	2.5	2.5	4.0	6.4	5.7	15.0	16.0
N <sub>2</sub> .....	57.0	55.3	2.0	58.9	52.5	56.0	46.7
O <sub>2</sub> .....	0.3	0.3	0.5	0.8	.....	0.4	0.1
B.t.u. ....	137	157	322	.....	.....	188	140

<sup>1</sup> Power, 40, 66.      <sup>2</sup> Made by the Hamler-Eddy Smoke Recorder Co., Chicago.

<sup>3</sup> Tech. Paper 106, Bureau of Mines, "Asphyxiation from Blast Furnace Gas."

<sup>4</sup> With 38.7% H<sub>2</sub>O, 3.2% ash.

<sup>5</sup> From "Gas Producers and Producer Gas Power Plants," R. D. Wood & Co., 1906.

<sup>6</sup> Richards, J. W., J. Frank. Inst., 415, 1900, quoted from V. Ihering, "Gas Maschinen."

GAS FROM DIFFERENT KINDS OF PRODUCERS

	Down Draft. <sup>1</sup>	Up Draft. <sup>2</sup>	Suction. <sup>1</sup>	Pressure, Taylor <sup>1, 3</sup>	Mond. <sup>1</sup>	Blast Furnace. <sup>4</sup>	Siemens. <sup>4</sup>
CO.....	17.5	18.3	26.0	22-30	16.0	24	28
H <sub>2</sub> .....	11.8	12.9	18.5	15-7	24.0	3	2
CH <sub>4</sub> .....	1.1	3.1	0.5	3-1.5	2.2	.....	.....
C <sub>2</sub> H <sub>4</sub> .....	.04	0.2	.....	.....	.....	2	2
CO <sub>2</sub> .....	9.2	9.8	8.0	6-1.5	12.4	12	3
N <sub>2</sub> .....	60.1	55.6	47.0	54-60	45.4	60	65
O <sub>2</sub> .....	0.2	.04	.....	.....	0	.....	.....
B.t.u. ....	110	.....	145	138	146	106	122

**Determination of Dust.** Liddell<sup>5</sup> recommends the following: lump sugar is crushed, and that which is retained by a 90-mesh sieve packed in a 2-in. layer upon copper or brass gauze contained in a glass tube. The sugar is slightly moistened and the gas sucked through it: it is then dissolved in water and the dust collected upon a tared Gooch crucible and weighed. Another procedure and apparatus recommended by the Sargent Steam Meter Co., of Chicago,<sup>6</sup> consists in sucking the gas through a diaphragm consisting of a weighed filter 4½ ins. in diameter, drying and noting the increase in weight.

### III. ILLUMINATING GAS<sup>7</sup>

The determinations usually made are as follows:

- |                     |                      |
|---------------------|----------------------|
| a. Candle power;    | e. Analysis;         |
| b. Calorific power; | f. Carbon dioxide;   |
| c. Sulphur;         | g. Specific gravity; |
| d. Ammonia;         | h. Tar.              |

(a) **Candle Power.** This can be very satisfactorily found using a 60-in. open-bar photometer and Leeson contrast disc. The gas should be burned from a burner commercially obtainable which gives the highest candle power; for gas from 14 to 21 candle power, Sugg's London argand burner, sizes C to F, should be used; for richer gases, Sugg's table top or the Bray slit burner. For a standard of comparison, the sperm candle is convenient, satisfactory, and very extensively used: the Elliott kerosene and Hefner amyl acetate lamps are also employed.

For accurate work the Lummer-Brodhun disc and electric standards, or the Hefner lamp should be used. For the determination of candle power, reference

<sup>1</sup> From "Gas Producers and Producer Gas Power Plants," R. D. Wood & Co., 1906.

<sup>2</sup> With anthracite buckwheat.

<sup>3</sup> "Résumé of Producer Gas Investigations," Bureau of Mines Bulletin 13, Fernald & Smith.

<sup>4</sup> Richards, J. W., J. Frank. Inst., 415, 1900, quoted from V. Ihering, "Gas Maschinen."

<sup>5</sup> Power, 88, 93.

<sup>6</sup> Power, 27, 331.

<sup>7</sup> Circular 48, Bureau of Standards, "Standard Methods of Gas Testing," 1916.

may be had to Circular No. 48 of the Bureau of Standards on "Standard Methods of Gas Testing," 1914, or Stone, "Practical Testing of Gas and Gas Meters," Wiley, 1909.

Carburetted water gas shows from 20-28 candle power, coal gas 14-20, oil gas 45-60, oil-air gas 30-35, gasolene 12-17, acetylene 170-200. (Stone, op. cit.)

(b) **Calorific Power.** (a) *Direct Determination.* This is most commonly

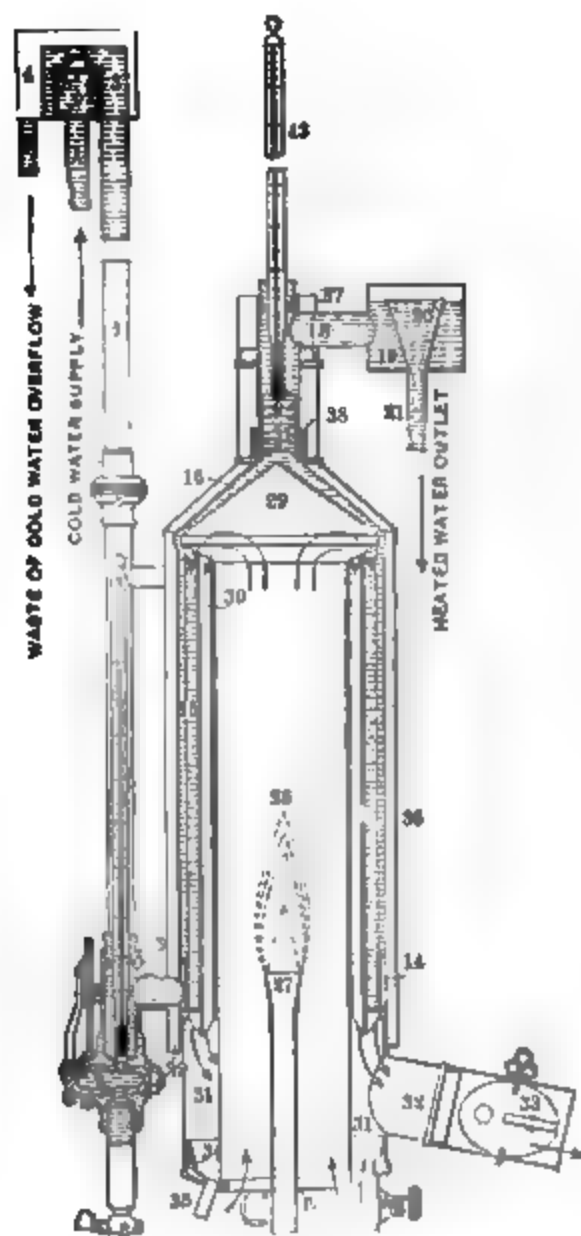


FIG. 124.

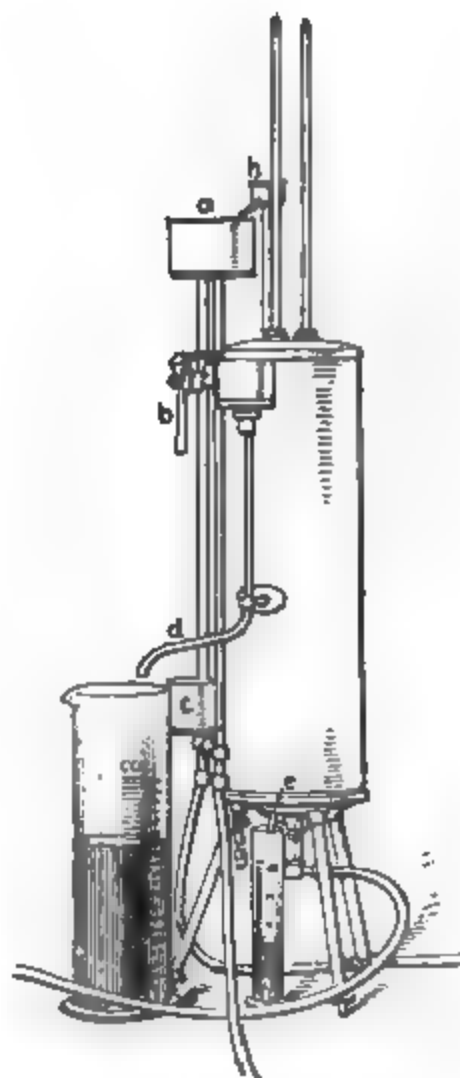


FIG. 125

determined by the Junkers calorimeter, although others in use are the Sargent, Doherty, and in England the Boys and Simmance-Abady.

The original form is shown in section in Fig. 124 and the later modification in Fig. 125. As seen in Fig. 124 it consists of a combustion-chamber, 28, surrounded by a water-jacket, 15 and 16, this being traversed by a great many tubes. To prevent loss by radiation this water-jacket is surrounded by a closed annular air-space, 13, in which the air cannot circulate. The whole apparatus is constructed of copper as thin as is compatible with strength. The water enters the jacket at 1, passes down through 3, 6, and 7, and leaves it at 21, while the hot combustion gases enter at 30 and pass down, leaving at 31. There is therefore



not only a very large surface of thin copper between the gases and the water, but the two move in opposite directions, during which process all the heat generated by the flame is transferred to the water, and the waste gases leave the apparatus approximately at atmospheric temperature. The gas to be burned is first passed through a meter, Fig. 126, and then, to insure constant pressure, through a pressure-regulator. The source of heat in relation to the unit of heat is thus rendered stationary; and in order to make the absorbing quantity of heat also stationary, two overflows are provided at the calorimeter, making the head of water and over-

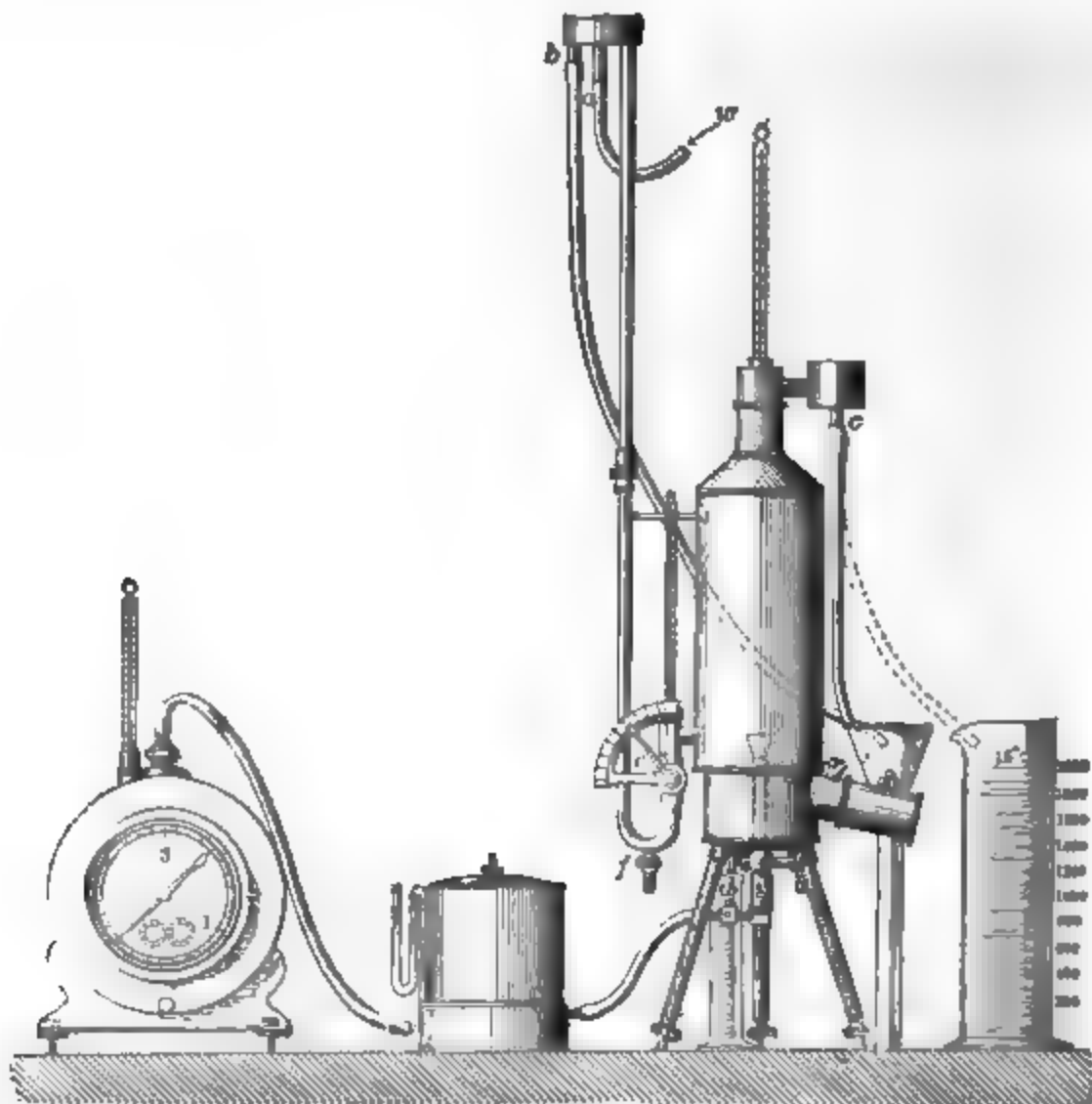


FIG 126.

flow constant. The temperatures of the water entering and leaving the apparatus can be read by 12 and 43; as shown before, the quantities of heat and water passed through the apparatus are constant. As soon as the flame is lighted 43 will rise to a certain point and will remain nearly constant.

**Manipulation.** The calorimeter is placed as shown in Fig. 126, so that the operator can simultaneously observe the two thermometers of the entering and escaping water, the index of the gas-meter, and the measuring-glasses.

No draft of air must be permitted to strike the exhaust of the spent gas.

The water-supply tube *w* is connected with the nipple *a* in the center of the upper container; the other nipple, *b*, is provided with a waste-tube to carry away the overflow, which latter must be kept running while the readings are taken.

The nipple *c*, through which the heated water leaves the calorimeter, is connected by a rubber tube with the large graduate. *d* empties the condensed water into the small graduate.

The thermometers being held in position by rubber stoppers and the water turned on by *e* until it discharges at *c*, no water must issue from *d* or from 39, Fig. 19, as this would indicate a leak in the calorimeter.

The cock *e* is now set to allow about two liters of water to pass in a minute, and a half, and the gas issuing from the burner ignited. Sufficient time, about twenty minutes, is allowed until the temperature of the inlet-water becomes constant and the outlet approximately so; the temperature of the inlet-water is noted, the reading of the gas-meter taken, and at this same time the outlet-tube changed from the funnel to the graduate. Ten successive readings of the out-flowing water are taken while the graduate (2-liter) is being filled and the gas shut off.

A better procedure is to allow the water to run into tared 8-liter bottles, three being used for a test, and weighing the water. The thermometer in the outlet can then be read every half-minute.

**Example.**—Temp. of incoming water, 17.2°  
 Temp. of outgoing water, 43.8°  
 Increase, 26.6°

Gas burned, 0.35 cu.ft.

$$\text{Heat} = \frac{\text{Liters water} \times \text{Increase of temp.}}{\text{Cu.ft. gas}} = \frac{2 \times 26.6}{0.35} = 152.3 \text{ C.}$$

From burning 1 cu.ft. of gas 27.25 cc. of water were condensed. This gives off on an average 0.6 C. per cc.

$27.25 \times 0.6 = 16.3 \text{ C.}$ ;  $152.3 - 16.3 = 136 \text{ C. per cubic foot}$ ;  $136 \times 3.968 = 540 \text{ B.t.u.}$

**NOTES.** After setting up the apparatus the first thing to be done is to turn on the water—(not the gas). Similarly, the water should be shut off last. All connections and the meter should be tested for leaks before each test. The water level in the meter should be checked daily. Slight drafts caused by moving suddenly near the apparatus will vary outlet readings and vitiate the test. The instrument should not be set up near a window or heating apparatus where radiant heat might affect the readings.

If 0.2 cu.ft. of gas are burned, then an error of 0.1° F. in temperature of water means an error of 4 B.t.u.; an error of 0.01 lb. water, 0.9 B.t.u.; 1° F. in gas temperature, 1.8 B.t.u.; 0.1 in. (barometer), 2 B.t.u.; 1 in. water pressure of gas, 1.5 B.t.u.<sup>1</sup>

The calorific power obtained without subtracting the heat given off by the condensation of the water represents the *total* heating value of the gas. This is the heat given off when the gas is used for heating water or in any operation where the products of combustion pass off below 100° C. The *net heating value* represents the conditions in which by far the greater quantity of gas is consumed, for cooking, heating and gas engines, and is one which should be reported. It should, however, be corrected,<sup>2</sup> to the legal cubic foot, that is, measured at 30 ins. barometric pressure, and 60° F. saturated with moisture.

The apparatus has been tested for three months in the German Physical Technical Institute with hydrogen, with but a deviation of 0.3% from Thomson's value. This

<sup>1</sup> Rept. Joint Committee on Calorimetry Public Service Commission and Gas Corporations in the Second Public Service District of New York State, p. 81, 1910.

<sup>2</sup> A difference of 1° C. or of 3 mm. pressure makes a change of 0.3% in the volume. Pfaffe, J. Gasbeleucht., 50, 67, 1907.

value may vary nearly that amount from the real value owing to the method which he employed.

The chief sources of error are,<sup>1</sup> in adjusting the meter, in measuring the temperature—rise of the water, and in changing over the outflow water to the weighed vessels.

(b) *By Calculation.*<sup>2</sup> Let us suppose an illuminating gas gave the following analysis: Illuminants 15, carbon monoxide 25.3, methane 25.9, hydrogen 27.9%; the heating value of these gases according to Table 3, page 737 is as follows:

$$\begin{array}{r}
 0.15 \times 2000 = 300.0 \text{ B.t.u.} \\
 0.253 \times 341 = 86.3 \\
 0.259 \times 1065 = 276.0 \\
 0.279 \times 345 = 96.3 \\
 \hline
 758.6 \text{ B.t.u.}
 \end{array}$$

which is the gross heating value of the gas. The correction for the heat lost is found as with chimney gases, by multiplying the volume of the combustion gases by their weight  $\times$  specific heat  $\times$  rise of temperature.

(c) *Sulphur.* Sulphur, being present in gas in so many forms, is determined by combustion and usually reported in grains of sulphur per hundred cubic feet.

One of the most easily portable and satisfactory forms is that of Hinman and Jenkins described as follows:<sup>3</sup> The upper vessel, Fig. 127, is a "bead glass" 300 mm. long and 60 mm. in diameter; this is filled with large cut-glass beads, held up by a suitable fluted glass, giving a large condensing surface without obstructing the draft. To this bead glass is attached, by a rubber connector, the adapter, 410 mm. long and 50 mm. lower internal diameter. To the upper adapter is attached, by means of the "connecting piece," the lower adapter, 400 mm. long and 40 mm. lower diameter. The connecting piece projects 12 mm. above the top of a rubber stopper, fitting the upper adapter, and is surmounted by a watch-glass deflector



FIG. 127. carried on platinum wires. An overflow tube carries the condensation to the Erlenmeyer flask hung on the stopper as shown; this tube is so adjusted that some liquid remains on the stopper to keep it cool and to absorb some of the ascending gases. The Bunsen burner is fitted with a lava tip having a 5-mm. hole; surrounding the burner is a glass tube 20 mm. in diameter, forming the inner wall of an annular chamber, of which the outer wall is a glass ring 50 mm. in diameter. Into this chamber, which serves to contain 10% ammonium hydroxide, the lower adapter dips 10 mm.

The lower adapter is joined to the "connecting piece" by a short cork-lined metal tube. Although radically different in form, this apparatus is very similar to the Referees' in general principle and in method of use, the principal difference

<sup>1</sup> Technologic Papers of the Bureau of Standards No. 36. "Gas Calorimetry," Waidner and Mueller, page 100, 1914.

<sup>2</sup> U. S. Geol. Survey Paper No. 48; Part III, page 1005.

<sup>3</sup> Jenkins, J. Am. Chem. Soc., 28, 543, 1906, also Technologic Paper No. 20, Bureau of Standards, McBride and Weaver "Determination of Sulphur in Illuminating Gas," 1913, also Stone, op. cit.

being the use of ammonium hydroxide instead of dry ammonium carbonate as a source of ammonia. About 10 cc. of concentrated ammonium hydroxide is placed in the reservoir about the burner at the beginning of the test and about 5 cc. more added every fifteen or twenty minutes. The gas is consumed at the rate of 0.4 to 0.6 cu.ft. per hour, and 2.5 to 3 ft. burned, if the sulphur is to be estimated gravimetrically, otherwise 1 cu.ft. is enough. When the run is completed the apparatus is allowed to cool and is then flushed four times by pouring 50 cc. portions of water in at the top of the bead tube. To the solutions and washings are added 2-3 cc. bromine water, and it is evaporated to 30 or 40 cc.; an excess of a hydrochloric acid solution of barium chromate is added to the hot solution, it is gently boiled, an excess of dilute ammonia added, again boiled for a minute, filtered and washed. The ammonium chromate in the filtrate (the chromic acid being equivalent to the sulphuric acid in the original solution) after being boiled in a stout flask, with a Bunsen valve, to expel the air, is cooled and titrated directly with stannous chloride (3.25 grams Sn per liter) using starch and potassium iodide to accentuate the end point.

The equations are:



The strength of the stannous chloride should be determined at the same time by standard bichromate of potassium.

Or the sulphuric acid can be determined with the turbidimeter as for sulphur in oils, page 570. The amount of sulphur is usually from 20 to 30 grains per 100 cu.ft.

**Sulphuretted Hydrogen.**<sup>1</sup> The test is made by hanging a strip of paper moistened with lead acetate solution (1 : 20) in a bell-jar or tube through which the gas is passing at about 5 cu.ft. per hour and allowing it to act for one minute. Usually several tests are made. The gas should be taken fresh from the main and care should be taken not to confound any black tarry spots with lead sulphide. A properly purified gas should give no test.

It is quantitatively determined by drawing a known volume of the gas through standard iodine solution. Tutweiler<sup>2</sup> measures the gas in a modified Bunte burette over mercury, and having added starch solution, runs in a known quantity of standard iodine solution until it is in slight excess. If 100 cc. of gas were taken, the number of cubic centimeters of solution gives the grains of  $\text{H}_2\text{S}$  per 100 cu.ft., 1 cc. iodine = 0.0017076 gram iodine = 100 grains  $\text{H}_2\text{S}$  per 100 cu.ft.

(d) **Ammonia.**<sup>3</sup> This is determined by absorption in standard acid colored with cochineal: 10 cc. of  $\text{HCl}$  are placed in the bulb, Fig. 117, 2-3 drops cochineal solution added, and the gas allowed to bubble through it until the yellow color changes to a deep purple; the meter is now read. The acid is made by diluting 38.2 cc.  $\text{N}/10$   $\text{HCl}$  to 1 liter, 10 cc. = 0.01 grain of  $\text{NH}_3$ ; the cochineal solution is made by treating 3 grams of the ground insect with 250 cc. 20% alcohol, allowing to stand forty-eight hours and filtering. The bubble tube is inserted in series

<sup>1</sup> Tech. Paper No. 41, Bureau of Standards, "Lead Acetate Test for Hydrogen Sulphide in Gas."

<sup>2</sup> J. Am. Chem. Soc., 23, 173, 1901.

<sup>3</sup> Tech. Paper No. 34, Bureau of Standards, "Determination of Ammonia in Illuminating Gas."

with the gas supply to the sulphur apparatus, Fig. 127, (c) so that both determinations are run at one time: the gas is passed through at the rate of 0.6 to 0.8 cu.ft. per hour. Massachusetts law limits the amount of ammonia to 10 grains per 100 cu.ft.

(e) **Analysis.** The volumetric analysis is carried out according to pages 704; either bromine water or fuming sulphuric acid can be used to absorb the "illuminants." Besides ethylene, it may be desirable to determine benzol: this is best done according to Dennis, O'Neill and McCarthy<sup>1</sup> by absorption in an ammoniacal solution of nickel cyanide.

**Naphthalene.** This is determined in purified gas by passing it through N/20 picric acid solution. White<sup>2</sup> determines it in raw gas by precipitation of the picrate and subsequent recovery of the naphthalene.

COMPOSITION OF COMMERCIAL GASES<sup>3</sup>

	CO <sub>2</sub>	H <sub>2</sub> O	O <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	N <sub>2</sub>	Candle Power.	B.t.u.
Coal...	1.6	4.0	0.4	8.5	49.8	29.5	3.2	3.2	16.1	622
Carb. water.....	3.0	13.3	0.4	30.4	37.7	10.0	3.2	2.1	22.1	643
Blue water.....	3.4	0.0	0.9	40.9	50.8	0.2	0.	3.5	.....	299
Pintsch .....	0.2	30.0	0.	0.1	13.2	45.0	9.0	1.6	43.0	1276
Blau. ....	0.	51.9	0.	0.1	2.7	44.1	0.	1.2	48.2	1704
Oil-water.....	2.6	7.0	0.2	9.2	39.8	34.6	..	6.6	19.7	690
Oil.....	0.3	31.3	0.	2.4	13.5	46.5	3.9	1.1	38.0	1320
Gasolene .....	..	1.5	18.5	..	..	C <sub>4</sub> H <sub>10</sub>	-10.3	69.7	16.0	514
Acetylene .....	..	96.0	0.8	..	..	.....	.....	3.2	225.0	1350
Natural .....	0.3	0.3	0.3	0.5	2.3	92.6	.....	3.5	$\frac{H_2S}{0.2}$	840-1170

(f) **Carbon dioxide.** This is best determined by Rudorff's method<sup>4</sup> which consists in titrating about a liter of the gas with standard potassium hydroxide. The arrangement and manipulation of this apparatus will be evident from Fig. 128: the capacity of the Woulff bottle must be known and if the gas contains hydrogen sulphide, it must be absorbed by passage over manganese dioxide.

(g) **Specific Gravity.** The readiest method depends upon the time of efflux of the gas compared with air;  $\text{sp.gr.} = \frac{G_1}{A_2} G$  and  $A$  represent the times of efflux in seconds of gas and air. The apparatus is obtainable from the dealers, or may be constructed according to Jenkins<sup>5</sup> as follows:

"It consists, Fig. 129, of two large rubber stoppers, each having a brass tube, projecting laterally near the large end, and connecting with the hole in the stopper. A glass piece  $A$  in the form of a truncated cone fits tightly over one stopper; it is 9 ins. long,  $1\frac{1}{2}$  ins. diameter at the base and 1 in. at the top. A similarly shaped piece  $B$  9 ins. long by  $1\frac{1}{2}$  ins. diameter at the lower end fits over the second stopper; 2 ins. above the latter the tube has a constriction 1 in. in diameter, and at its

<sup>1</sup> J. Am. Chem. Soc., 30, 236, 1908.

<sup>2</sup> Proc. Mich. Gas Association, 83, 1904, 1905.

<sup>3</sup> Fulweiler, Rogers' and Aubert's, "Industrial Chemistry," 2d Ed., 404.

<sup>4</sup> Orton, Geol. of Ohio, VI, 137.

<sup>5</sup> Hempel, op. cit., 262.

<sup>6</sup> Stone, op. cit., 261. See also Bureau of Standards, Tech. Papers 89 and 94, by J. S. Edward.

upper part is narrowed to a neck  $\frac{1}{8}$  in. in diameter which is ground on the inside to receive the end of a tube  $7\frac{1}{2}$  ins. long and  $\frac{1}{2}$  in. in diameter, in the upper end of which is fitted a platinum plate containing the emission orifice. One and three-fourths inches below this plate is a three-way glass stopcock, and 3 ins. below the latter a scratch surrounds the tube and serves as the upper mark in the escape of the gas.

"Fitted into the hole in the stopper is a hollow cylinder of brass to which is soldered a curved piece of brass wire pointed at the end, which rises  $1\frac{1}{2}$  ins. above the surface of the stopper. The two brass tubes projecting from the outside of the stoppers are joined by a piece of rubber tubing 15 to 18 ins. long.

"In using this instrument the larger tube *B* is filled with water, of the temperature of the room, nearly to the top, the stopcock being turned so that egress



FIG. 128.



FIG. 129.

of air from the smaller tube is prevented. The larger tube is placed on an elevated surface just high enough so that its bottom is above the level of the scratch on the narrow outlet tube, the cock is turned so that the air may escape through the orifice in the platinum plate, and on the second, when the point of the brass wire breaks the surface of the rising water, a stop watch is started. The latter is stopped when the water exactly reaches the scratch.

"The large tube is lowered, and the stopcock turned so that air may enter through its hollow point. When the water is again all in the large cylinder, the cock is turned to connect the small vessel with the outside air through the platinum tip, the large cylinder is replaced on the elevation and the operation repeated. Results should be obtained which check within one-fifth second.

"Now connect a rubber tube to the gas supply and to the tip of the stopcock, lower the large cylinder and force the water into the latter by means of the gas pressure. Thoroughly saturate the water with the gas to be tested; this may be done by shaking gas and water together and by forcing the water up and down in the small vessel in contact with the gas. Repeat the operation with gas in the same manner as described for air. The calculation is made in accordance with the formula.

"The advantages of this apparatus are its portability, its cheapness, its rapidity and accuracy. When set up, the cylinders are inclined to be a trifle unstable; this may be overcome by fastening a lead plate to the base of each stopper. Four precautions in connection with its use should be emphasized: (1) The water must be of the room temperature; (2) the water must be thoroughly saturated with the gas; (3) the platinum tip, stopcock, and upper part of the tube must be kept dry and clean; (4) the large cylinder must always, in any one determination, be placed at the same height."

Another method consists in the use of the Lux gas balance. This consists of a balanced globe into which the gas previously filtered through cotton, passes and its specific gravity is read off directly on a scale.

The knowledge of the specific gravity is important, as it is involved in the formula for the calculation of the flow of gas in pipes; it also enables the gas manager to ascertain the weight of gas produced from the coal, and to get an idea of the nature and amount of impurities in the gas, all these being heavier.

(h) **Tar.** For the estimation of tar, Clemens Winkler<sup>1</sup> recommends the procedure of Tiefftrunk: This consists in passing the gas through 25% alcohol and collecting and weighing the tar on a tared filter.

#### IV. SULPHURIC ACID GASES,

the gases involved in the manufacture of sulphuric acid:

- a. Burner gases;
- b. Nitrogen gases;
- c. Oxygen;
- d. Gases involved in the contact process.

##### (a) Burner Gases. Sulphur Dioxide

This gas may be determined by the method of Reich. It consists in aspirating the gas through standard iodine solution (N/10 is suitable) until it is decolorized. The amount of iodine used in the test and the volume of the aspirated gas being known, the percentage of  $\text{SO}_2$  can readily be calculated.

Fig. 130 shows a form of apparatus for making this determination. The standard iodine, 5 to 25 cc. N/10 I, diluted to 150 to 200 cc., is placed in the bottle, about 400 cc. capacity, and starch indicator added.<sup>2</sup> The gas to be tested is aspirated through the iodine until the color of the starch blue fades completely. Water which flows out from the graduated cylinder by lowering the aspirating bottle, produces the suction, and the amount measures the volume of the aspirated gas. From the quantity of iodine used and the volume of the gas required to decolorize the solution the per cent of sulphur dioxide is calculated.

<sup>1</sup> "Die Industrie Gase," page 52, also Hempel, op. cit., 239.

<sup>2</sup> Starch indicator may be omitted if the light is good for observing the fading out of the iodine color.

Should the contact gas contain SO<sub>2</sub>, this is absorbed by passing the gas through 50 to 100 cc. of strong H<sub>2</sub>SO<sub>4</sub>, to avoid the action of SO<sub>2</sub> on the rubber tubing of the apparatus. A rapid current of the gas is passed through the acid to saturate it with SO<sub>2</sub> before making the tests.

The Reich method is more applicable for determining small amounts of SO<sub>2</sub>. A 12-15-liter graduated aspirating bottle is used in works tests of exit gases for measuring the gas. Since these volumes are under standard conditions (760 mm. and 0° C.), it will be necessary to convert the volumes obtained in the tests to these conditions, using the formula  $V = V^o \frac{P^o - w}{760 (1 + 0.00367t)}$ , where  $V^o$  = measured volume,  $P^o$  = observed barometric pressure,  $t$  = temperature of the gas, and  $w$  = aqueous vapor pressure at temperature of the test.

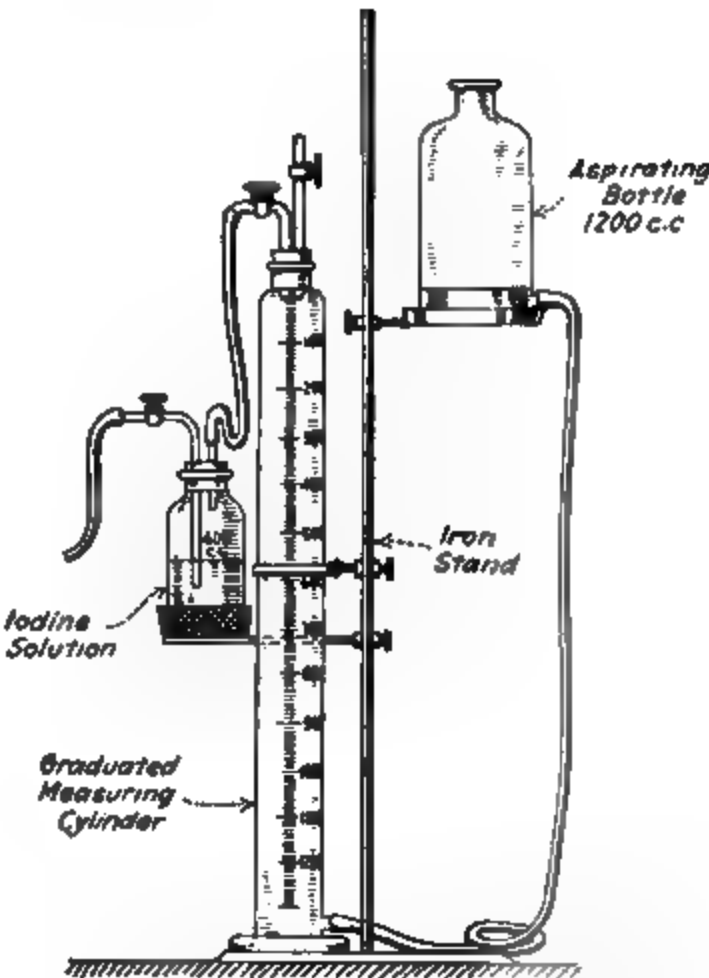


FIG. 130. Portable Reich Apparatus.

TABLE FOR REICH'S TESTS FOR PERCENTAGE SO<sub>2</sub>. USING TENTH NORMAL IODINE SOLUTION

Volume Per cent SO <sub>2</sub>	25 cc. N/10 Iodine.	10 cc. N/10 Iodine.	5 cc. N/10 Iodine.
12	205 cc. gas	.....	.....
11.5	215 " "	.....	.....
11	226 " "	.....	.....
10.5	238 " "	.....	.....
10	252 " "	.....	.....
9.5	265 " "	.....	.....
9	283 " "	.....	.....
8.5	300 " "	.....	.....
8	321 " "	.....	.....
7.5	344 " "	.....	.....
7	371 " "	148 cc. gas	.....
6.5	402 " "	161 " "	.....
6	438 " "	175 " "	.....
5.5	.....	192 " "	.....
5	.....	212 " "	.....
4.5	.....	237 " "	.....
4	.....	268 " "	.....
3.5	.....	308 " "	154 cc. gas
3	.....	361 " "	181 " "
2.5	.....	436 " "	218 " "
2	.....	.....	274 " "
1.5	.....	.....	367 " "
1.4	.....	.....	393 " "
1.3	.....	.....	424 " "
1.25	.....	.....	442 " "



**Sulphur Dioxide in Exit Gases.**<sup>1</sup> Sulphur dioxide is seldom above 1% in exit gases leaving the absorption tower of the sulphuric acid plant. Generally the loss is below 0.2% on a carefully regulated unit. The Reich method is sufficiently accurate for this determination, for all practical purposes. If 10 cc. of N/10 iodine are used the percent SO<sub>2</sub> may be calculated by the formula:

$$\frac{11.17}{V_0 + 11.17} = \% \text{SO}_2$$

$V_0$  = volume of the gas reduced to standard condition 0° C and 760 mm.

11.17 = cc. of SO<sub>2</sub> gas equivalent to 10 cc. of N/10 iodine.

The following table is calculated on the assumption that the gas is under a pressure of 760 mm. + vapor pressure of 17 mm., at room temperature of 20° C.

Measured Vol.	Per cent SO <sub>2</sub>	Measured Vol.	Per cent SO <sub>2</sub>
1000 cc.	1.22	3200 cc.	.38
1100 cc.	1.09	3400 cc.	.36
1200 cc.	1.01	3600 cc.	.34
1300 cc.	.93	3800 cc.	.32
1400 cc.	.87	4000 cc.	.31
1500 cc.	.81	4200 cc.	.29
1600 cc.	.76	4400 cc.	.28
1700 cc.	.72	4600 cc.	.27
1800 cc.	.67	4800 cc.	.26
1900 cc.	.64	5000 cc.	.25
2000 cc.	.61	5500 cc.	.22
2100 cc.	.58	6000 cc.	.20
2200 cc.	.55	6500 cc.	.18
2300 cc.	.53	7000 cc.	.17
2400 cc.	.51	7500 cc.	.16
2500 cc.	.49	8000 cc.	.15
2600 cc.	.47	8500 cc.	.14
2700 cc.	.45	9000 cc.	.14
2800 cc.	.44	9500 cc.	.13
2900 cc.	.42	10000 cc.	.12
3000 cc.	.41		

### Sulphur Dioxide in the Inlet Gases of the Sulphuric Acid Contact System<sup>1</sup>

**Apparatus. Burette.** This should be of the bulb type with a graduated capacity of 100 cc., the bulb holds about 87 cc.; the stem is graduated in tenths of a cubic centimeter from 0 to 12 cc. The diameter of this graduated portion is such that each cubic centimeter occupies approximately 18 mm. in length. The total length of the burette is 45 to 50 cc.

There is a constriction at the lower end of the burette, or the rubber tube connecting the burette with the leveling tube may be pinched down so that it requires 10 to 15 seconds to pass 100 cc. of mercury in or out of the burette.

The burette has a water jacket of sufficient capacity to include the chamber of the burette and its graduated portion. The diameter should be sufficient to accommodate the bulbed portion of the burette and a thermometer suspended by its side. Distilled water boiled free of air is used in this water jacket.

<sup>1</sup> Communicated by W. W. Scott

A thermometer registering from 5 to 35° graduated in tenths of a degree is left suspended in the water jacket next to the bulb.

*Leveling Tube.* This is preferably a straight glass cylinder constricted at lower end to accommodate the heavy-walled rubber tubing, connecting the tube with the burette. This tube is about 52 cm. long and has a diameter of 18 to 25 mm. The lower portion of the tube, where this is held by the hand, has a covering either of rubber, or of a heat-insulating material, to prevent warming of the mercury while making the test.

*Capillary Tube.* The tube connecting the burette with the pipettes and the

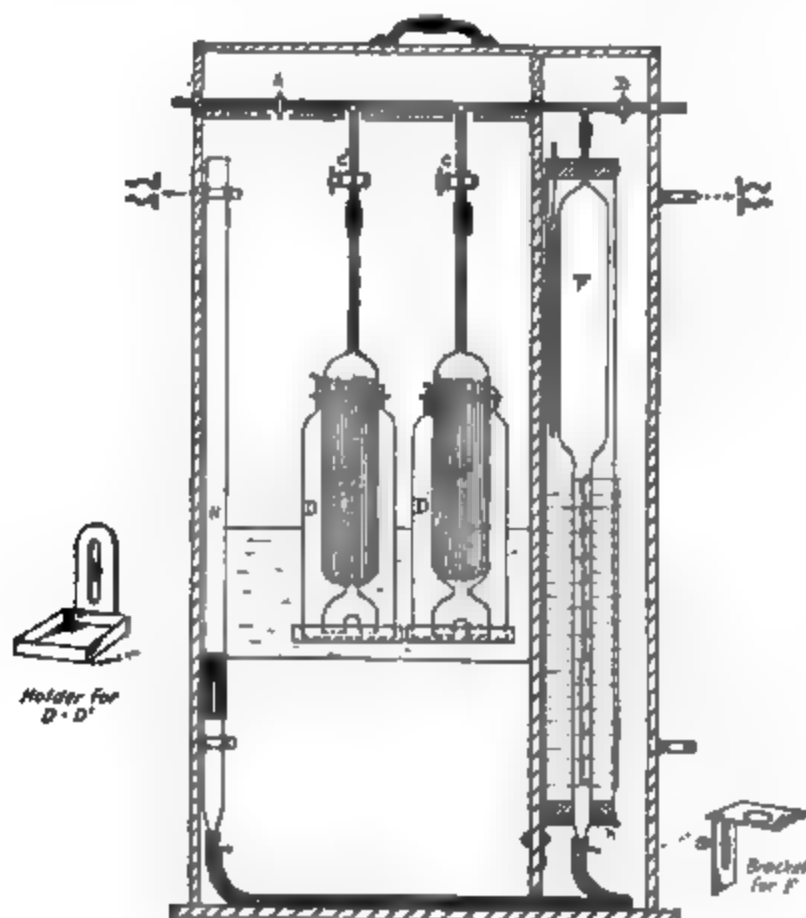


FIG. 131.<sup>1</sup>

sampling pipe should have a fine capillary—the entire internal capacity should not exceed 1 cc. Details of construction shown in the figure.

*Pipette.* The cylinder of the pipette has a capacity of 150 to 175 cc. The pipette reservoir of 500 to 550 cc. capacity is recommended.

*Reagents. Mercury.* Mercury is used in the measuring burette. This should be kept bright and clean and "drag no tail." To keep the gas saturated with moisture the burette should contain about 0.2 cc. of distilled water over the mercury.

*Water Solution of Chromic Acid.* A 50% solution is recommended, although a weaker solution may be used. The strength of the reagent, however, should be over 25%  $\text{CrO}_3$ .

*Sampling.* The iron pipes carrying the gas to and from the testing apparatus have a diameter of  $\frac{1}{4}$  in. to  $\frac{1}{2}$  in. The line is run from the positive pressure

<sup>1</sup> Orsat apparatus modified by T. L. Briggs and W. W. Scott

flue near the blower to the testing apparatus and back to the minus pressure flue entering the blower, and the gas allowed to flow continuously through this shunt line.

**Making the Test.** A volume of 100 cc. of the gas is drawn into the chamber burette (Fig. 131), by opening the stopcock *A* (*B* being closed) and lowering the leveling-tube—Stopcock *A* is closed, *B* opened and the gas expelled into the air by raising the leveling tube *H*, using care to prevent mercury bumping at the top of the reservoir. (Mercury carried into the chromic acid will reduce this reagent.) A second 100 cc. of the gas is taken and expelled as before. Finally a third 100 cc., carefully measured, is taken for the test. The top of the mercury columns in the burette and leveling tubes should be exactly level. The water surface should be at the 0 mark on the burette. Stopcock *B* is always closed during the drawing in of the gas. The temperature of the water jacket is now observed. Stopcock *A* is closed and stopcock *C* leading to the absorption pipette opened. The leveling tube is raised as before and the gas completely passed into the pipette. The gas is drawn back into the measuring burette by lowering the leveling tube and measured. The mercury columns should stand at the same level, the reading being taken at the surface of the water over the mercury. A second pass into the pipette is now made and, if no further contraction of the gas occurs, the reading taken. The temperature is observed and a correction made of 0.36 cc. per degree (centigrade) rise or fall of temperature. This correction is added if the temperature rises, or is subtracted if the temperature falls.

The contraction of the gas, due to absorption of  $\text{SO}_2$ , in terms of cc. gives the direct per cent reading.

**Example:**

100 cc. gas taken.  
Final reading 91.5, i.e., direct = 8.5 cc.  
Temperature change =  $0.4^\circ$  rise.  
Then  $8.5 + (.4 \times .36) = 8.6\% \text{ SO}_2$ .

Tests should be made in duplicate, each Orsat having two pipettes. Very little more time is required to run the check test if the following method is observed. The first sample is taken and passed into one of the pipettes; a second sample, immediately taken, is passed into the second pipette. The first sample is now again measured and then returned to the first pipette and then the check sample measured and returned to its pipette. The first sample is again measured and if a further contraction is observed it is again passed into its pipette and the process repeated with the second sample. By thus alternating the tests and allowing the gas to stand in the pipettes the second pass will cause complete absorption of  $\text{SO}_2$ , third pass seldom being necessary.

**Notes and Precautions.** *Burette.* The constriction preventing a rapid flow of mercury accomplishes the following:

1. It prevents the wave motion of mercury, which results from a rapid flow. This wave motion makes it exceedingly difficult to draw in 100 cc. of gas accurately, and makes it necessary to hold the tube several seconds until the motion has ceased before taking a reading.

2. The constriction prevents mercury bumping into the capillary and from being thus carried into the absorption reagent.

3. It minimizes the danger of drawing the absorption reagent into the chamberette.

*Water in the Burette.* The burette should, as stated, always contain about 2 cc. of water, over the mercury to saturate the gas with moisture. Results 1 to  $\frac{1}{2}\%$  low will be obtained if the burette is allowed to become dry, the amount of error depending upon the temperature of the gas. One hundred cc. of dry gas expand upon absorbing moisture to 101.2 cc. at 10°; 101.7 cc. at 15°; 102.3 cc. at 20°; 103.1 cc. at 25° and 104.1 cc. at 30°.

*Leveling Tube.* The covering recommended prevents warming of the mercury with the hand. When the apparatus is kept stationary, practically no change of temperature takes place during the test if the mercury is thus protected, so that a temperature correction will not be required. If the apparatus is moved from a warm to cold zone or vice versa, temperature corrections will become necessary.

*Pipette.* The form of pipette shown in the illustration is simple and compact. The bottle affords both protection and acts as a water jacket. The pipette is filled with thin-walled tubes having a small bore. The pipette should be tightly packed as loose packing and large-bored tubes both lessen the efficiency of the pipette, cutting down the surface for absorption.

*Rubber Tube Connection.* Since sulphuric anhydride acts on rubber, in presence of this gas, rubber tubing for connecting the testing apparatus to the sampling pipe should not be used, except in flush connections with the pipe in contact with the inlet tube of the apparatus. In absence of sulphuric anhydride the use of rubber tubing is not objectionable.

*Cleaning the Burette upon Accidental Drawing in of Chromic Acid.* Should the reagent be accidentally sucked into the capillary or into the burette, it may be easily washed out with distilled water by drawing this through stopcock *B* and flushing out several times by lowering and raising the leveling tube. The excess water may be removed from the capillary by opening stopcock *C* and allowing to flow out. If mercuric oxide is formed in the burette it may be dissolved by flushing with sodium hydroxide solution.

*Chromic Acid Reagent.* Theoretically, a charge of 50% aqueous chromic acid solution (100 g.  $\text{CrO}_3 + 100 \text{ g. H}_2\text{O}$ ) amounting to 300 cc., is sufficient to absorb the  $\text{SO}_2$  of over 12,000 determinations. In practice, however, the reagent should be renewed long before the chromic acid has been used up by the sulphurous acid.

*Number of Passes.* Although two passes are generally sufficient to completely absorb the  $\text{SO}_2$ , it is necessary to make a third pass and observe whether any further contraction takes place. If the reagent is effective and there are no leaks in the apparatus the third pass will show no change.

*Lubrication of Stopcocks.* A mixture of beeswax and vaseline or wool grease (1 : 2) has been found excellent for this purpose. Not only does it lubricate the stopcock, but it prevents leaks. Eighty parts rubber melted with 20 parts beeswax is also good and is acid resisting.

*Rubber Tube Connections.* Coating the glass tube with a viscous solution of sealing wax, dissolved in alcohol, or etching it with hydrofluoric acid, on the portion covered by the rubber will make a tight joint so that wiring the joint will not be necessary.

*Parallel Leveling Lines* are placed behind the burette to enable more accurate leveling of the mercury columns.

## (b) Nitrogen Oxides

Nitrogen tetroxide,  $N_2O_4$ , and nitrous acid,  $N_2O_3$ , can best be determined by absorption in standard permanganate (acidulated with sulphuric acid) according to p. 694.

Nitric oxide can be determined by passing the gases through soda lye, then by adding air to the collected volume, converting it to nitrogen tetroxide and determining it as above indicated.

Nitrous oxide is determined in the acid-free gases by explosion with hydrogen.

(c) Oxygen is usually determined by acid or ammoniacal cuprous chloride—phosphorus is also employed. The percentage of oxygen should not exceed six; a larger amount means that heat is being lost from the chambers by the exhaust gases. Knowing their temperature, the loss of heat can be calculated as with chimney gases.

V. MINE GASES<sup>1</sup>

The gases to be sought are those found in illuminating gas and for most purposes the procedure on p. 1248 can be followed. For small quantities of methane the apparatus of Haldane, modified and described by Burrell and Seibert<sup>2</sup> should be used. This is practically an Orsat, using mercury as the confining liquid and with a compensating tube and grisometer for burning the methane.

For determination of methane alone, the apparatus of Shaw<sup>3</sup> may be recommended. This determines first the per cent of illuminating gas necessary to make an explosion of definite strength with ordinary air; when this has been done, mine air is used in place of the ordinary air and a smaller percentage of illuminating is required—smaller by the amount of combustible gas in the mine air. The strength of the explosion is measured by noting by the ear the force with which the plunger is driven out from the explosion cylinder against a bell.

In case this apparatus be not at hand, Brunck's<sup>4</sup> method can be employed. This consists in burning the methane in a 2-liter Erlenmeyer flask by means of an electrically heated platinum spiral. The flask carrying the spiral in the stopper is sunk inverted in a vessel of water and the current allowed to pass for half an hour, which is sufficient to burn the methane. It is then cooled and 25 cc.  $BaO_2H_2$  (1 cc. = 1 cc.  $CO_2$ ) added, time allowed for absorption of the carbon dioxide and the excess of  $BaO_2H_2$  determined, p. 728, and the quantity of methane calculated.

Clowes and Redwood<sup>5</sup> have worked out a method for the detection of inflammable gas in air, employing the "flame cap." When an inflammable atmosphere is brought in contact with a candle or better a hydrogen flame, the gas burns, forming a "cap," like the colorless flame above the blue cone in a Bunsen burner the length of the flame is a measure of the percentage of gas, and as little as 0.1% is visible using the hydrogen flame.

**Carbon Monoxide.** Besides combustible gases or "fire damp," it is sometimes necessary to get an idea of the amount of carbon monoxide ("white damp")

<sup>1</sup> See Technical Paper 14, Bureau of Mines, "Apparatus for Gas Analysis Laboratories at Coal Mines."

<sup>2</sup> Bull. 42, U. S. Bureau of Mines, 17, 42, 1913, also Technical Paper 39, 13.

<sup>3</sup> Berichte, 27, 692.

<sup>4</sup> O. Brunck, "Die Chem. Unters. d. Grubenwetter," 1908.

<sup>5</sup> "Detection and Estimation of Inflammable Gas and Vapor in the Air," 1896 also Clowes, J. Soc. Arts, 41, 307. Also McTrusty, "Mine Gases and Gas Testing," 191

in the mine air after an explosion or in the "after damp"; chemical methods, p. 704, being too slow, use is made of the behavior of birds and mice when exposed to such an atmosphere. To this end they are carried in cages by the rescuing party and their behavior noticed. Canaries show distress in an atmosphere containing 0.15% of CO in five to twelve minutes, or with 0.20% in half this time: Mice are less sensitive,<sup>1</sup> and men may display distress when carbon monoxide is as little as 0.1%, whereas animals may be unaffected. In case either is overcome by the gas, resuscitation can be effected by bringing them out into the open air again. Repeated exposure of the gas would seem to be without influence.

## VI. ELECTROLYTIC GASES

Gases from electrolytic chlorine, hydrogen and oxygen generators. The following are to be sought for:

(a) Chlorine, (b) oxygen, (c) carbon dioxide, (d) carbon monoxide, (e) hydrogen.

(a) Chlorine. Hempel<sup>2</sup> recommends measuring the gas quickly in his burette over water and then sucking in 5 cc. of 50% potassium iodide solution through the capillary and shaking; the diminution in volume gives the chlorine.

The other gases are determined in the usual way. As phosphorus cannot be used for pure oxygen, a specially prepared potassium pyrogallate, p. 735, is employed; cuprous chloride or ammoniacal cuprous carbonate in the absence of carbon monoxide is very satisfactory.

## VII. ACETYLENE

Commercial acetylene may contain the following gases:

- |              |                              |
|--------------|------------------------------|
| 1. Oxygen;   | 4. Nitrogen;                 |
| 2. Hydrogen; | 5. Sulphur-containing gases; |
| 3. Methane;  | 6. Phosphine.                |

Oxygen is estimated after the absorption of the acetylene itself in fuming sulphuric acid, in the usual way with potassium pyrogallate. Methane and hydrogen would be determined in this residue, after treatment with ammoniacal cuprous chloride to complete the removal of acetylene, by the ordinary explosion methods, p.1248. Nitrogen would be left as a residue.

Sulphur-containing gases. These are most likely organic sulphides, as hydrogen sulphide is probably absent, since the solution is strongly alkaline from which the acetylene escapes. They can be determined by combustion, as in illuminating gas, p. 1260, and best be reported as "total sulphur."

Phosphine is also similarly estimated and the phosphoric acid determined in the usual way: the quantity of PH<sub>3</sub> rarely exceeds 0.05%. Acetylene can be purified by passing over bleaching powder, through acid cuprous chloride or chromic acid: The candle power is usually given as fifty per cubic foot, or 180-200, when burned at the rate of 5 cu.ft. per hour. The explosive limits are, according to Clowes<sup>3</sup> 3 to 82%, to Burrell and Oberfell, 2.5 to 73%.<sup>4</sup>

<sup>1</sup> Burrell, Seibert and Robertson, Bureau of Mines Technical Paper 62, 1914, "Relative Effects of Carbon Monoxide on Small Animals." Also Tech. Paper 11.

<sup>2</sup> "Gas-Analytische Methoden," 4th Ed., 1913, p. 278.

<sup>3</sup> Op. cit.

<sup>4</sup> Bureau of Mines Tech. Paper 112, "Explosibility of Acetylene."

## VIII. ATMOSPHERIC AIR

(a) Moisture; (b) Carbon dioxide; (c) Ozone; (d) Carbon monoxide; (e) Bacteria.

(a) **Moisture**<sup>1</sup> by chemical means, see p. 1275. The amount of moisture can be determined by the sling psychrometer, or wet- and dry-bulb thermometer or by the hair hygrometer. The sling psychrometer is the most rapid and accurate—the wet- and dry-bulb thermometers are so arranged that they can be rapidly whirled for fifteen or twenty seconds, stopped and quickly read, the wet bulb first; this is repeated until closely agreeing readings are obtained. The humidity is determined in the usual manner from the meteorological tables.

The amount of moisture in the air is probably indirectly responsible for our sensations of comfort or discomfort, rather than the amount of carbon dioxide, as was formerly thought. This moisture controls the heat loss from the body, which loss must be normal—neither too high nor too low. The greater the humidity the less the evaporation, consequently the less the cooling.

For comfort, the higher the temperature the less should be the humidity; the following shows the relation between the two:

Temp., °F. ....	60	68 <sup>2</sup>	70	80	90
Relative humidity, per cent	67	40	49	31	16

(b) **Carbon Dioxide.** One of the most satisfactory methods is that of Hesse.<sup>3</sup> This consists in absorbing the carbon dioxide from a definite volume of air with standard barium hydroxide and determining its loss of strength.

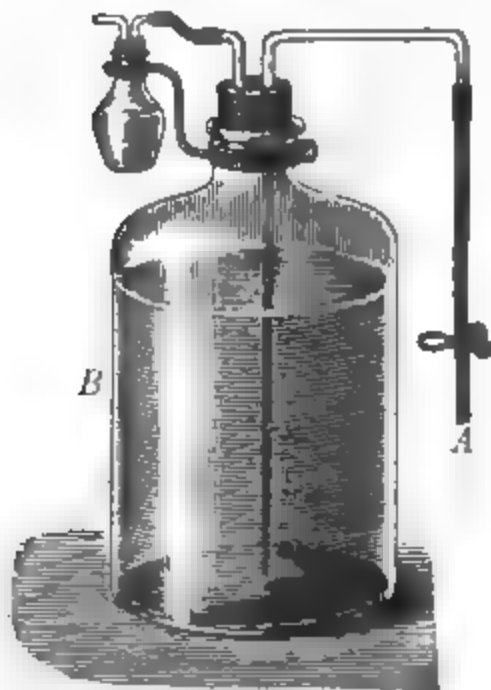


FIG. 132.

The air is collected in heavy Erlenmeyer flasks of 100–500 or 1000 cc. capacity, or clear glass bottles; these are stoppered with doubly perforated rubber stoppers carrying glass plugs and the capacity of the flask or bottle noted to the depth of the stopper. A 10-cc. pipette and a 15-cc. glass-stoppered burette graduated in cc./10 with an 8-cm. tip, complete the outfit; a solution of 1.7 grams of barium hydroxide and chloride (20 : 1) in a liter of water, *B* Fig. 132, and of oxalic acid 5.6325 grams per liter (1 cc. = 1 cc. CO<sub>2</sub>), with phenolphthalein 1 : 250, are required.

The bottles are filled with steam by exposure for three minutes and the vaselined stoppers inserted, or they may be filled with distilled water and opened in the place the air of which is to be examined.

In all this work, it should be remembered that the exhaled breath contains about 400 parts carbon dioxide per 10,000, consequently care should be taken not to contaminate the samples, nor should they be warmed with the hand.

The 10-cc. pipette is partly filled from the tube *A*, Fig. 132, by means of the rubber connector and sucking the liquid into the pipette: it is rinsed, filled and

<sup>1</sup> Benedict, "The Composition of the Atmosphere with Special Reference to its Oxygen Content," Carnegie Institution of Washington, 1912, Publication No. 166.

<sup>2</sup> For indoor work. <sup>3</sup> Eulenberg's Vierteljahrschr. f. ger. Med. u. San. N. F., 31, 2.

inserted through one of the holes in the rubber stopper of the bottle, the other plug being momentarily opened. The plugs are replaced and the bottles allowed to rest on their sides, with occasional rolling, for twenty minutes. Not more than one-fifth of the solution should be used up by the carbon dioxide present.

During this time, the barium hydroxide should be standardized; to this end a few drops of phenolphthalein and a quantity of the oxalic acid almost sufficient to neutralize the hydroxide should be run into a 100-cc. Erlenmeyer flask from the burette; this should be passed through the doubly perforated stopper; 10 cc. of the barium hydroxide solution are run into the flask as above described, and also the oxalic acid until a pink color appears.

Phenolphthalein is added to the bottles containing the samples, the oxalic acid burette inserted through the stopper and the excess of barium hydroxide titrated.

The barometric pressure and temperature in the laboratory are noted and the volume of the bottle less 10 cc. ( $\text{BaO}_2\text{H}_2$ ) calculated to standard conditions; the difference in the titer of the barium hydroxide solution gives the volume of carbon dioxide in the bottle; this is calculated into parts per 10,000.

Other methods for this determination are more strictly gasometric, measuring the diminution in volume by absorption: Benedict<sup>1</sup> used Sonden's, and Anderson<sup>2</sup> recommends a shortened form of the Pettersson-Palmquist apparatus.

This may be described as an Orsat apparatus using mercury instead of water and with a 25-cc. burette the lower part of which is graduated to 0.0025 cc.; this is connected to a pipette of potassium hydroxide, a delicate manometer and compensating tube. The apparatus is delicate and rapid, but requires a skilled operator to manipulate it.

The amount of carbon dioxide in the outdoor air in the city is about 3.1 parts per 10,000, in the house, 3.7-3.9; with 6-7 parts in a room, the ventilation may be considered as excellent, with 10 parts as about the upper limit. In some theaters which were lighted by gas it approached 50 parts.

(c) **Ozone.** Probably most conveniently determined by Wurster's method, p. 1241.

*Determination of Ozone Iodide Method of Schönbein.*<sup>3</sup> The method depends upon the reaction



**Procedure.** A glass bulb of 300 cc. to 400 cc. capacity (the exact capacity being determined by weighing empty, then full of water) with two tubes at opposite sides, closed by stopcocks, one of which was a three-way cock, is filled with water. The ozone tested is introduced into the vessel, displacing the water. The gas is brought to atmospheric pressure by quickly opening and closing one of the cocks. A solution of 2N potassium iodide is introduced in excess of that required, through the three-way cock by means of a second bulb connected by rubber tube to the vessel, after displacing the air in the rubber connection through the cock. The mixture is well shaken and allowed to stand half an hour. The contents of the bulb are washed out with additional iodide solution followed by distilled water and the liberated iodine titrated with standard thiosulphate.

1 cc. N/10  $\text{Na}_2\text{S}_2\text{O}_3$  = 0.0024 g.  $\text{O}_3$ .

<sup>1</sup> Op. cit.

<sup>2</sup> J. Am. Chem. Soc., 25, 162, 1913.

<sup>3</sup> Further details of this method may be found in Treadwell and Hall "Quantitative Analysis."



(d) **Carbon Monoxide.** The qualitative detection is most certainly effected by the blood test: to this end the gas is drawn through a solution of blood contained in a Wolff, Fig. 115, or similar absorption tube and examined for its absorption spectrum. The blood solution is made by mixing ox blood which has been defibrinated by whipping, with an equal quantity of a cold saturated solution of borax; this can be kept (as a side-shelf reagent) in the laboratory for months. This solution is diluted with 19 volumes of water, giving a solution of blood of 1 in 40 which is placed in the absorption tube. The air is drawn through it at a rate of 3 liters per hour, requiring 10 liters in some cases: the solution is put in a thin flat-sided bottle and spectroscopically examined.

Pure diluted blood, Fig. 133, shows two dark absorption bands, spectrum 2, between the D and E line: these are welded into one broad band by reducing agents as  $\text{NH}_4\text{SH}$ , spectrum 4: blood which has absorbed carbon monoxide shows two broader bands in the same place, spectrum 3, which are unaffected by reducing agents. The quantitative determination depends upon the equation,



This has been studied by Kinnicutt and Sanford<sup>1</sup> and recently by Morgan and McWhorter<sup>2</sup> and by the writer. The process consists in sucking the air through the iodine pentoxide contained in a U-tube heated in cottonseed oil or glycerin bath to  $150^\circ$ , passing the iodine into potassium iodide solution and then absorbing

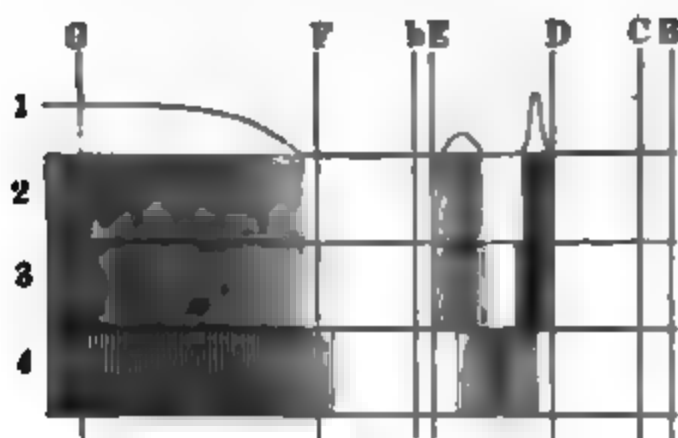


FIG. 133.

the carbon dioxide in standard barium hydroxide. Both the iodine and barium hydroxide solutions are titrated. The last two investigators call particular attention to the ease with which iodine pentoxide at  $150^\circ$  is decomposed by organic matter, particularly stopcock grease; the pentoxide should be sealed into the U-tube, as glass stopcocks cannot be used. The writer can substantiate this statement, and would suggest further that the U-tube be chemically

cleaned with cleaning solution ( $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ ) before filling with  $\text{I}_2\text{O}_5$ , as well as the tubes through which the gas is sucked before reaching the U-tube; rubber connections should, if possible, be avoided, and the tubing should have been cleansed by warming with dilute soda lye and washing. The U-tube should be drawn down to the same size as the connecting glass tubing and the two butted closely together in the cleansed rubber connector.

The iodine is titrated with  $\text{N}/1000$  thiosulphate and every 2.27 mg. of iodine corresponds to 1 cc. of carbon monoxide under standard conditions; the carbon dioxide is absorbed in the hydroxide contained in a long test-tube  $24 \times 2.5$  cm. and titrated with oxalic acid (1.1265 grams crystallized acid to 1 liter) using phenolphthalein; 5 cc. of the acid are equivalent to 1 cc. of carbon dioxide.

Haldane<sup>3</sup> states that as little as .01% of carbon monoxide can be determined colorimetrically by absorbing in diluted blood and comparing it with standard carmine solution; carbon monoxide turns the brownish yellow color of the blood to pink.

(e) **Bacteria.** See "Standard Methods for Bacterial Examination of Air." Am. J. Pub. Health, 6, No. 3, 1910.

<sup>1</sup> J. Am. Chem. Soc., 22, 14, 1900. <sup>2</sup> Ibid., 29, 1589, 1907. <sup>3</sup> Clowes, op. cit., 1-23

## DETERMINATION OF MOISTURE IN GASES

The gas to be tested is passed through a dehydrating agent such as phosphorus pentoxide,  $P_2O_5$ , alumina,  $Al_2O_3$ , or lime,  $CaO$ , contained in a weighed U-tube, Fig. 134.

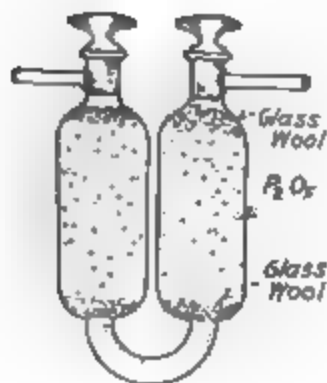


FIG. 134.

The following facts should be borne in mind in selecting the dehydrating agent: (a) It should not absorb the gas; (b) it should not react chemically with the gas. For example—lime or alumina could not be used for determining moisture in sulphur dioxide, nor could phosphorus pentoxide be used in determining moisture in ammonia. For the former, phosphorus pentoxide is best, and for the latter, lime. Alumina that has been carefully heated to  $1400^\circ$  is useful for determining moisture in neutral gases. It should be remembered that gases dried over calcium chloride will give up moisture to strong sulphuric acid, and these in turn will give up

moisture to phosphorus pentoxide: Professor Morley has even determined the amount of moisture that is left after this latter treatment.

**Procedure.** The volume of the gases required for the test varies widely according to the percentage of moisture in the gas, 1000 cc. to 10,000 cc. are generally required. For minute amounts of moisture it may be necessary to lead the gas over the dehydrating agent for a given length of time, using a manometer or difference gauge, or a gas meter. The absorption tube is weighed before and after the test and the increase in weight taken as the moisture content of the gas.

**Method of Determining Gasolene Vapor in Gaseous Mixtures.**<sup>1</sup> Fig. 135 shows the apparatus for the gasolene-vapor determination. The bulb *a* contains phosphorus pentoxide for removing water vapor. If the latter were not removed it would also be retained at low temperatures and would subsequently exert pressure when measurement was being made of the pressure exerted by the gasolene vapor.

To start a determination the apparatus is connected to a vacuum pump and its air exhausted. The mixture of gasolene vapor and air is then introduced at atmospheric pressure, the barometer is read, and the two bulbs are immersed in liquid air contained in a Dewar flask. After about ten minutes, the air is removed from the apparatus with a vacuum pump. The stopcock on the apparatus is then closed, the liquid air in the Dewar flask removed, the gasolene allowed to vaporize, and its pressure read on the mercury manometer attached to the apparatus. The ratio of this pressure to the pressure of the atmosphere gives the percentage of gasolene vapor originally in the air.

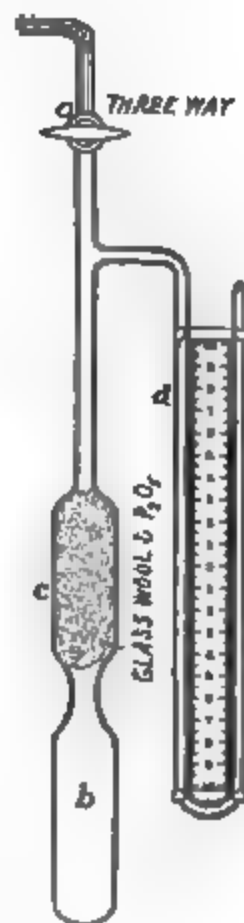


FIG. 135.

<sup>1</sup> U. S. Bureau of Mines, Technical Paper No. 115, Burrell and Boyd.

### DETERMINATION OF NITROGEN BY THE NITROMETER<sup>1</sup>

The nitrometer, Fig. 136, consists of a gas-generating bulb fitted at the top with a two-way cock leading to a dissolving cup and a gas-exit tube, and which has at the bottom a connection for a rubber tube leading to a leveling tube, the whole being filled with mercury to a level just below the upper cock; a cylindrical glass measuring tube graduated from 0–100 cc. connected to a leveling tube through

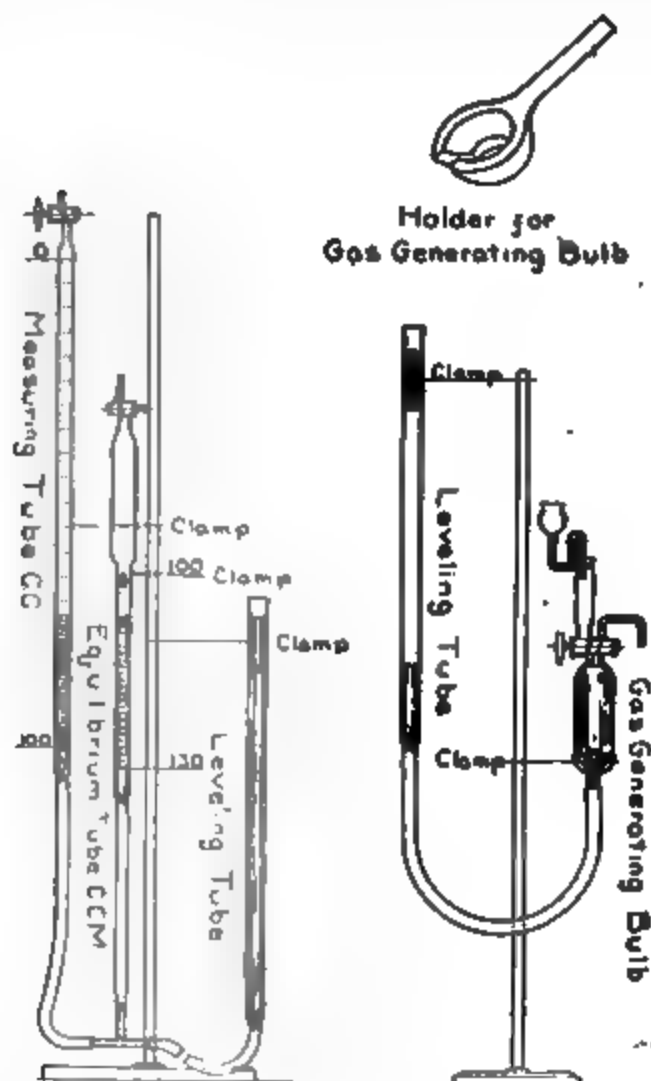


FIG. 136.

a T-tube leading to an equilibrium tube. The latter is shaped like an inverted 100-cc. pipette graduated downward below the bulb from 100–130 cc. The whole system is filled with mercury so that the measuring tube may be completely discharged by raising the leveling tube.

*Adjusting the Equilibrium Tube.* The volume of 100 cc. of dry air at 0° C. and 760 mm. under the temperature and barometric conditions prevailing at the time is calculated, 3 drops of 98% sulphuric acid are drawn into the tube, and the level of the mercury fixed in accordance with the calculation. The cock of the tube is then closed and sealed with melted paraffin. The volume in this tube may be confirmed at any time by opening the measuring tube and adjusting the leveling tube so that the level is the same in the three tubes. The volume of gas in the equilibrium tube is then read and compared with the calculated volume

<sup>1</sup> Joyce and La Tourette, J. Ind. and Eng. Chem. 5, 1017, 1913.

at the time, a correction in the subsequent gas readings in the measuring tube being made accordingly.

*Nitrogen in Potassium Nitrate.* Approximately 0.4 gram potassium nitrate is placed in a weighing tube, dried two hours at 110° C., desiccated twenty-four hours over sulphuric acid and weighed exactly by difference into the cup of the gas-generating bulb. This is dissolved in 9 cc. 95% sulphuric acid, added through a siphon thistle tube, entering the top of the dissolving cup through a tight-fitting rubber stopper. When the salt is dissolved it is drawn into the gas-generating bulb and followed by two washings 1.5 cc. each of 95% acid. The bulb is then shaken with a motion normal to its long dimension until the volume of gas determined by a rough paper scale pasted on the leveling tube becomes constant, this operation taking from three to five minutes.

The gas is passed into the measuring tube, and after standing five minutes the leveling and measuring tubes are so adjusted that the level in the equilibrium tube reads 100 cc. and is the same as the level in the measuring tube. The reading of the latter is then taken. As the temperature and barometric conditions, in so far as they affect the measured volume of the gas, are automatically compensated by the equilibrium tube, and as the gas is washed with sulphuric acid and is, therefore, dry, the percentage of nitrogen may be calculated directly, correcting only for the calibration of the equilibrium and measuring tubes. Seventeen determinations made when the room temperature ranged from 20-28° gave 13.71% nitrogen, the theoretical being 13.84%.

The nitrometer gives reliable results within 0.02% in nitrate nitrogen, using 0.4-0.5 gram sample. It is not available for the determination of nitrogen in celluloid or other substances containing carbon ring compounds which appear to prevent the complete liberation of nitric oxide in the presence of sulphuric acid and mercury.

Besides the corrections for calibration and standardization of the nitrometer in accordance with temperature and barometer, the gas readings should be corrected for solubility of nitric oxide, which diminishes when the temperature goes above 28° C., and the formation of other gases by the breaking up of the cellulose molecule which increases.

The following table gives the algebraic sum of these two corrections for temperatures ranging from 20° to 35° C.

Temp.	Co.	Temp.	Co.
20.0-27.5	+0.90	30.0	-0.14
28.0	+0.74	30.5	-0.70
29.0	+0.34	31.0-35.0	-0.94

## REAGENTS AND TABLES

The reagents used in gas analysis, particularly in the absorption apparatus, are comparatively few and easily prepared.

**Hydrochloric Acid**, Sp. gr. 1.10. Dilute "muriatic acid" with an equal volume of water. In addition to its use for preparing cuprous chloride, it finds employment in neutralizing the caustic solutions which are unavoidably more or less spilled during their use.

**Fuming Sulphuric Acid**. Saturate "Nordhausen oil of vitriol" with sulphuric anhydride. Ordinary sulphuric acid may be used instead of the Nordhausen; in this case about an equal weight of sulphuric anhydride will be necessary. *Absorption capacity*, 1 cc. absorbs 8 cc. of ethene (ethylene).

**Acid Cuprous Chloride**. The directions given in the various text-books being troublesome to execute, the following method, which is simpler, has been found to give equally good results: Cover the bottom of a two-liter bottle with a layer of copper oxide or "scale"  $\frac{1}{2}$  in. deep, place in the bottle a number of pieces of rather stout copper wire reaching from top to bottom, sufficient to make a bundle an inch in diameter, and fill the bottle with common hydrochloric acid of 1.10 sp.gr. The bottle is occasionally shaken, and when the solution is colorless, or nearly so, it is poured into the half-liter reagent bottles, containing copper wire, ready for use. The space left in the stock bottle should be immediately filled with hydrochloric acid (1.10 sp.gr.).

By thus adding acid or copper wire and copper oxide when either is exhausted, a constant supply of this reagent may be kept on hand.

The *absorption capacity* of the reagent per cc. is, according to Winkler, 15 cc. CO; according to Hempel 4 cc. The author's experience with Orsat's apparatus gave 1 cc.

Care should be taken that the copper wire does not become entirely dissolved and that it extend from the top to the bottom of the bottle; furthermore the stopper should be kept thoroughly greased the more effectually to keep out the air, which turns the solution brown and weakens it.

**Ammoniacal Cuprous Chloride**. The acid cuprous chloride is treated with ammonia until a faint odor of ammonia is perceptible; copper wire should be kept in it similarly to the acid solution. This alkaline solution has the advantage that it can be used when traces of hydrochloric acid vapors might be harmful to the subsequent determinations, as, for example, in the determination of hydrogen by absorption with palladium. It has the further advantage of not soiling mercury as does the acid reagent.

*Absorption capacity*, 1 cc. absorbs 1 cc. CO.

Cuprous chloride is at best a poor reagent for the absorption of carbonic oxide; to obtain the greatest accuracy where the reagent has been much used, the gas should be passed into a fresh pipette for final absorption, and the operation continued until two consecutive readings agree exactly. The compound formed by the absorption possibly  $\text{Cu}_2\text{COCl}_2$  is very unstable, as carbonic oxide may be freed from the solution by boiling or placing it *in vacuo*; even if it be shaken up with air, the gas is given off, as shown by the increase in volume and subsequent diminution when shaken with fresh cuprous chloride.

**Hydrogen**. A simple and effective hydrogen generator can be made by joining two 6-in. calcium chloride jars by their tubulatures. Pure zinc is filled

in as far as the constriction in one, and the mouth closed with a rubber stopper carrying a capillary tube and a pinchcock. The other jar is filled with sulphuric acid 1 : 5 which has been boiled and cooled out of excess of air. The mouth of this jar is closed with a rubber stopper carrying one of the rubber bags used on the simple pipettes.

**Mercury.** The mercury used in gas analysis should be of sufficient purity as not to "drag a tail" when poured out from a clean vessel. It may perhaps be most conveniently cleaned, except from gold and silver, by the method of J. M. Crafts, which consists in drawing a moderate stream of air through the mercury contained in a tube about 3 ft. long and  $1\frac{1}{4}$  ins. internal diameter. The tube is supported in a mercury-tight V-shaped trough, of size sufficient to contain the metal if the tube breaks, one end being about 3 ins. higher than the other. Forty-eight hours' passage of air is sufficient to purify any ordinary amalgam. The mercury may very well be kept in a large separatory funnel under a layer of strong sulphuric acid.

Or Meyer's method<sup>1</sup> may be used. A separatory funnel is used to hold the mercury. The delivery tube of the funnel is slightly narrowed 0.5 cm. from the lower end. Over this side is bound with twine a piece of rather closely woven muslin. The mercury is allowed to flow through the cloth into a solution of mercury nitrate contained in a tall cylinder, with stopcock at the lower end. The tip of the funnel with the muslin dips under the surface of the cleaning solution. The purified mercury is drained off from the bottom of the cylinder. It can also be purified except from traces of zinc by distillation.

**Palladous Chloride.** Five grams palladium wire are dissolved in a mixture of 30 cc. hydrochloric and 2 cc. nitric acid, this evaporated just to dryness on a water bath, redissolved in 5 cc. hydrochloric acid and 25 cc. water, and warmed until solution is complete. It is diluted to 750 cc. and contains about 1% of palladous chloride. It will absorb about two-thirds of its volume of hydrogen.

**Phosphorus.** Use the ordinary white phosphorus cast in sticks of a size suitable to pass through the opening of the tubulated pipette.

**Potassium Hydrate.** (a) For carbon dioxide determination, 500 grams of the commercial hydrate are dissolved in 1 liter of water.

*Absorption capacity.* One cc. absorbs 40 cc. CO<sub>2</sub>.

(b) For the preparation of potassium pyrogallate for special work, 120 grams of the commercial hydrate are dissolved in 100 cc. of water.

**Potassium Pyrogallate.** Except for use with the Orsat or Hempel apparatus, this solution should be prepared only when wanted. The most convenient method is to weigh out 5 grams of the solid acid upon a paper, pour it into a funnel inserted in the reagent bottle, and pour upon it 100 cc. of potassium hydrate (a) or (b). The acid dissolves at once, and the solution is ready for use.

If the percentage of oxygen in the mixture does not exceed 28, solution (a) may be used;<sup>2</sup> if this amount be exceeded, (b) must be employed. Otherwise carbonic oxide may be given off even to the extent of 6%.

Attention is called to the fact that the use of potassium hydrate purified by alcohol has given rise to erroneous results.

*Absorption capacity.* One cc. absorbs 2 cc. O.

<sup>1</sup> J. H. Hilderbrand, J. Am. Chem. Soc., 31, 934.

<sup>2</sup> Clowes, Jour. Soc. Chem. Industry, 15, 170.

**Sodium Hydrate.** Dissolve the commercial hydrate in three times its weight of water. This may be employed in all cases where solution (a) of potassium hydrate is used. The chief advantage in its use is its cheapness. Sodium pyrogallate is, however, a trifle slower in action than the corresponding potassium salt.

TABLE 1

TABLE SHOWING THE TENSION OF AQUEOUS VAPOR AND ALSO THE WEIGHT IN GRAMS CONTAINED IN A CUBIC METER OF AIR WHEN SATURATED

From 5° to 30° C.

Temp.	Tension, mm.	Grams.	Temp.	Tension, mm.	Grams.	Temp.	Tension, mm.	Grams.
5	6.5	6.8	14	11.9	12.0	23	20.9	20.4
6	7.0	7.3	15	12.7	12.8	24	22.2	21.5
7	7.5	7.7	16	13.5	13.6	25	23.6	22.9
8	8.0	8.1	17	14.4	14.5	26	25.0	24.2
9	8.5	8.8	18	15.4	15.1	27	26.5	25.6
10	9.1	9.4	19	16.3	16.2	28	28.1	27.0
11	9.8	10.0	20	17.4	17.2	29	29.8	28.6
12	10.4	10.6	21	18.5	18.2	30	31.5	29.2
13	11.1	11.3	22	19.7	19.3			

**Moisture in the Air.**<sup>1</sup> Twenty tests made on different days extending from October 17th to November 10th, 1916, at a period agreeing closely with the average atmospheric conditions, gave results varying from 0.1510 gram to 0.5031 gram water vapor per standard cubic foot. The average of the results was 0.2469 gram moisture per cubic foot of air. Omitting three rainy days of this period the average moisture of the air in the laboratory (75° F.) was found to be 0.2141 gram per cubic foot.

It is an interesting fact that at 75° F., 52 per cent sulphuric acid (recommended as a standard) is in equilibrium with air containing 0.2137 gram moisture per cubic foot, according to an average of results by W. W. Scott and a calculation from Sorel's table on tension of aqueous vapor in mixtures of sulphuric acid and water.

TABLE 2

SPECIFIC HEATS OF GASES AT CONSTANT VOLUME

	Volumetric. <sup>1</sup>	
Air.....	0.243	0.019
Carbon dioxide.....	0.234	0.027
Carbonic oxide.....	0.245	0.019
Hydrogen.....	3.41	0.019
"Illuminants".....	0.404 <sup>2</sup>	0.040
Methane.....	0.593	0.027
Nitrogen.....	0.244	0.019
Oxygen.....	0.217	0.019
Aqueous vapor.....	0.480	.....

The "volumetric" specific heat is the quantity of heat necessary to raise the temperature of 1 cu.ft. of gas from 32° F. to 33° F.

<sup>1</sup> Communicated by W. W. Scott.

<sup>2</sup> H. L. Payne, Jour. Anal. and Applied Chem., 7, 233.

<sup>3</sup> Ethylene.

TABLE 3

CALORIFIC POWER OF VARIOUS GASES<sup>1</sup> IN BRITISH THERMAL UNITS PER CUBIC FOOT

Name.	Symbol.	60° F. Initial.	32° F. Initial. 32° F. Final.	Ignition Point °F.
Hydrogen.....	H <sub>2</sub>	326.2	345.4	1085 <sup>4</sup>
Carbonic oxide.....	CO	323.5	341.2	1200 <sup>4</sup>
Methane.....	CH <sub>4</sub>	1009.2	1065.0	1230
Illuminants <sup>2</sup> .....			2000.0	.....
Ethane.....	C <sub>2</sub> H <sub>6</sub>	1764.4	1861.0	1140
Propane.....	C <sub>3</sub> H <sub>8</sub>	2521	2657.0	1015
Butane.....	C <sub>4</sub> H <sub>10</sub>	3274	3441.0	.....
Pentane.....	C <sub>5</sub> H <sub>12</sub>	.....	4255.0	.....
Hexane <sup>3</sup> .....	C <sub>6</sub> H <sub>14</sub>	.....	5017.0	1400
Ethylene.....	C <sub>2</sub> H <sub>4</sub>	1588	1674.0	1010 <sup>4</sup>
Propylene.....	C <sub>3</sub> H <sub>6</sub>	2347.2	2509.0	940
Benzene.....	C <sub>6</sub> H <sub>6</sub>	3807.4	4012.0	.....
Acetylene.....	C <sub>2</sub> H <sub>2</sub>	1476.7	1477.0	788 <sup>4</sup>

TABLE 4

1 pound	=453.59 grams	1 calorie	=3.969 B.t.u.
1 cubic inch	=16.39 cc.	1 cubic meter	=35.31 cu.ft.
1 cubic foot	=28.315 liters		
1 B.t.u. per cu.ft.	=8.89 calorie per cubic meter	1 calorie per cu. meter	=0.1124 B.t.u. per cu.ft.
1 in. H <sub>2</sub> O pressure	=1.87 mm. Hg pressure	1 mm. Hg pressure	=0.535 in. H <sub>2</sub> O pressure

#### Acetylene

Absorbents—Fuming sulphuric acid. Ammoniacal cuprous chloride produces a red color. Used as qualitative test.

#### Ethylene (in presence of Acetylene)

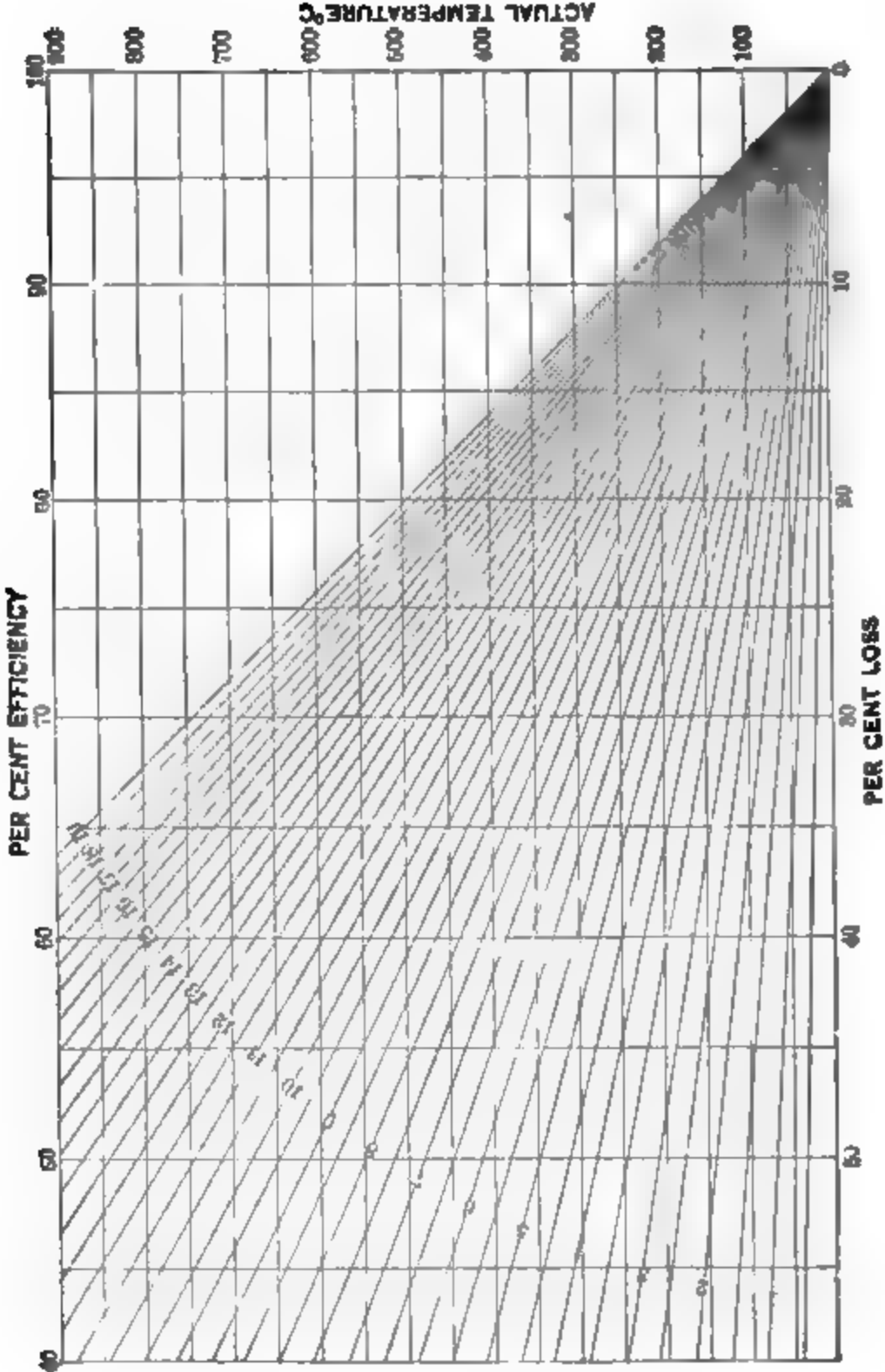
Absorbent—Fuming sulphuric acid absorbs Acetylene and Ethylene. Cold bromine or iodine sol. Ethylene not attacked. Hence determined both by H<sub>2</sub>SO<sub>4</sub>+SO<sub>2</sub> and Ethylene by Br. Diff. = Acetylene.

#### Benzene

Absorbent—Fuming sulphuric acid. Bromine water + Br. CO<sub>2</sub> is first absorbed by KOH (saturated with benzene vapor), then benzene in fuming sulphuric acid.



TABLE 5  
BUNTE'S CHART



## DETERMINATION OF SULPHUR DIOXIDE IN THE ATMOSPHERE<sup>1</sup>

This method is used for the determination of less than 10 and will detect as little as 0.1 part of sulphur dioxide per million by volume.

Determinations can be made in the field at the rate of one every 5 minutes.

The method depends upon measuring the bleaching effect of the sample of atmosphere on starch iodide solution by the amount of standard iodine solution required to restore the tint to that of an equal quantity of the same solution which has been treated mechanically in a barren atmosphere in the same way and under the same conditions in respect to temperature, light, kind and surface area of glassware.

Two aspirator bottles of 20 to 24 liters capacity each are employed; one (*B*), the exact volume of which is known, is the holder in which the sample is measured and treated with starch iodide solution; the other (*A*) is a check bottle in which a barren atmosphere is treated with an equal portion of the starch iodine solution. The two bottles should be of the same sort of glass and of approximately the same capacity.

Bottle *A*, the check bottle, has a solid rubber stopper in the upper tubulure and in the lower, a rubber stopper with a  $\frac{3}{8}$ -inch hole (*b*) which is closed by a glass plug (*a*). The glass plug should fit so it will retain liquid in the bottle but can be removed with little effort.

Bottle *B*, the sample bottle, has the upper tubulure fitted with a rubber stopper having a  $\frac{3}{8}$ -inch hole closed permanently by a glass stopcock (*c*) tube. The lower tubulure is outfitted in a similar manner, but the stopcock (*g*) tube must fit not so firmly in the hole (*b*) that it cannot be easily pulled out.

The titrating bottles (*C* & *D*) should be alike and of clear white glass. Bottles  $2\frac{1}{2}$  inches diameter,  $6\frac{3}{4}$  inches high and fitted with No. 8 rubber stoppers are suitable. The stopper to each of these bottles have each a 2 or 3 mm. bore vent tube (*d*), a  $\frac{3}{8}$ -inch L tube (*e*) which must not extend beyond the surface of the stopper inside of the bottle and must fit the holes (*b*) in the lower tubulures of the aspirator bottles. The  $\frac{3}{8}$ - to  $\frac{1}{2}$ -inch hole (*f*), which is closed by the forefinger or by a glass plug during a part of the process of determination, may have inserted in it a  $\frac{1}{2}$ -inch glass tube as the finger seat. These bottles should be marked in some way to distinguish the one from the other.

The mixing bottle (*E*) of about 500 cc. capacity is kept free of dust by a rubber stopper.

The 10 or 15 cc. burette for the iodine solution should have a long delivery tube so that the iodine may be discharged through the hole (*f*) clear of the stopper.

The vacuum pump is the type having a plunger barrel  $2\frac{1}{2}$  by 16 inches.

The vacuum gauge should be provided with a scale upon which are marks indicating the vacuum to be attained corresponding to the temperature prevailing.

The method of making this calculation so that burette readings may be converted directly to parts per million by volume is formulated as follows:

$$F = \frac{I}{\frac{MV}{B} \times \frac{B}{B'} \times \frac{T'}{T' + T}},$$

<sup>1</sup> Report of the Selby Smelter Commission, Bulletin 98, Bureau of Mines.

where  $F$  = Fraction of volume it is desired that each cc. of the iodine solution shall correspond to in terms of cc. of  $\text{SO}_2$  at 0/760.

$I$  = Volume equivalent of 1 cc. of the iodine solution in terms of cc. of  $\text{SO}_2$  at 0/760.

$M$  = Volume in cc. of the space for gas in the aspirator bottle in which the sample of atmosphere is taken.

$B$  = Barometer reading in mm. of mercury.

$B' = 760$ .

$V$  = Vacuum in mm. of mercury.

$T$  = Temperature, Centigrade.

$T' = 273$ .

Examination of the equation shows that barometric pressure is without influence in the calculation. The simplified equation is

$$\frac{FMVT'}{B'(T' + T)} = I. \quad \text{Since } \frac{T'}{B'} = \frac{273}{760} = 0.36, \text{ then } \frac{0.36FMV}{T' + T} = I.$$

When the gas capacity of the aspirator bottle is, for example, 21000 cc.,  $7560FV = I(T' + T)$ .

When the fraction desired to be represented by 1 cc. of the iodine solution is the equivalent in volume of  $\text{SO}_2$  to 2 parts per million, then 0.000002 ( $7560FV$ )  $I(T' + T)$ , then  $0.01512V = I(T' + T)$ .

By substituting 380 for  $V$  and the average temperature in degrees Cent. for  $T$  in this equation, the strength of iodine solution suitable to the size of aspirator bottle and fraction may be found.

When the fraction desired is 2 parts per million and the aspirator has a volume of 20 to 28 liters, it is convenient to use the N/500 solution.

When N/500 iodine solution is used,  $0.01512V = 0.0224T' + 0.0224T = 6.1152 + 0.0224T$ , then  $V = 405 - 1.48T$ .

Because of the tediousness of the operation and possible injury by a collapsed bottle it is not good practice to evacuate above 500 mm.

To establish uniform reducing conditions internally, the bottles should be prepared for analytical work by washing their inner surfaces and the plugs with sulphuric acid-bichromate of potassium solution (300 cc. of O.V. plus a few grams of  $\text{K}_2\text{Cr}_2\text{O}_7$ ) and then with distilled water until free of the oxidizing fluid. Both tubulures are now closed to the atmosphere by their corresponding plugs. 300 to 400 cc. of starch solution are poured into the mixing bottle (which must be kept closed and free of dust), and given a light lavender tint by the addition of 1 to 2 cc. of N/500 iodine solution. (Note: The quality of the starch solution is a matter of supreme importance in the operation of this method. Made in the following manner, it retains its sensitiveness throughout a working day: 1 gram of soluble starch is made into a paste by triturating with a few cc. of cold water and this paste is added to 1 liter of cold distilled water which contains 2 grams of potassium iodide. The liquid is brought just to boiling and then quickly cooled by setting the beaker into cold water. It is the practice to make up a fresh batch each day.) The starch solution is divided equally between the two titration bottles and from each transferred to the corresponding aspirator. The transfer is made by pulling out the glass rod or stopcock tube from the hold (b), inserting (e), closing (f) tightly with the

forefinger or with a glass plug, inverting the titration bottle by turning (e) around in the hole (b) and at the same time tilting back somewhat the aspirator. The appropriate glass rod and tube plugs are then replaced and both aspirators shaken for an equal length of time (2 minutes) under the same conditions respecting light and so that every portion of each bottle receives an equal amount of wetting. Each solution is now transferred to its titration bottle by tilting back the aspirator, pulling the plug in the hole (d), inserting (e) and with (f) open tilting forward the aspirator until all of the starch solution has run into the titration bottle. The hole (b) is then closed with its corresponding glass plug. If, on comparing the solutions against a white background, both are of the same tint, the aspirators are considered ready for use in the field. If the colors are not the same, the test solutions are mixed (more iodine added if the bleaching has been great), halved and transferred to the aspirators in the same manner as before. The aspirators are shaken and the solutions again compared. The operation should be repeated until the iodine consumption factor is the same for both bottles.

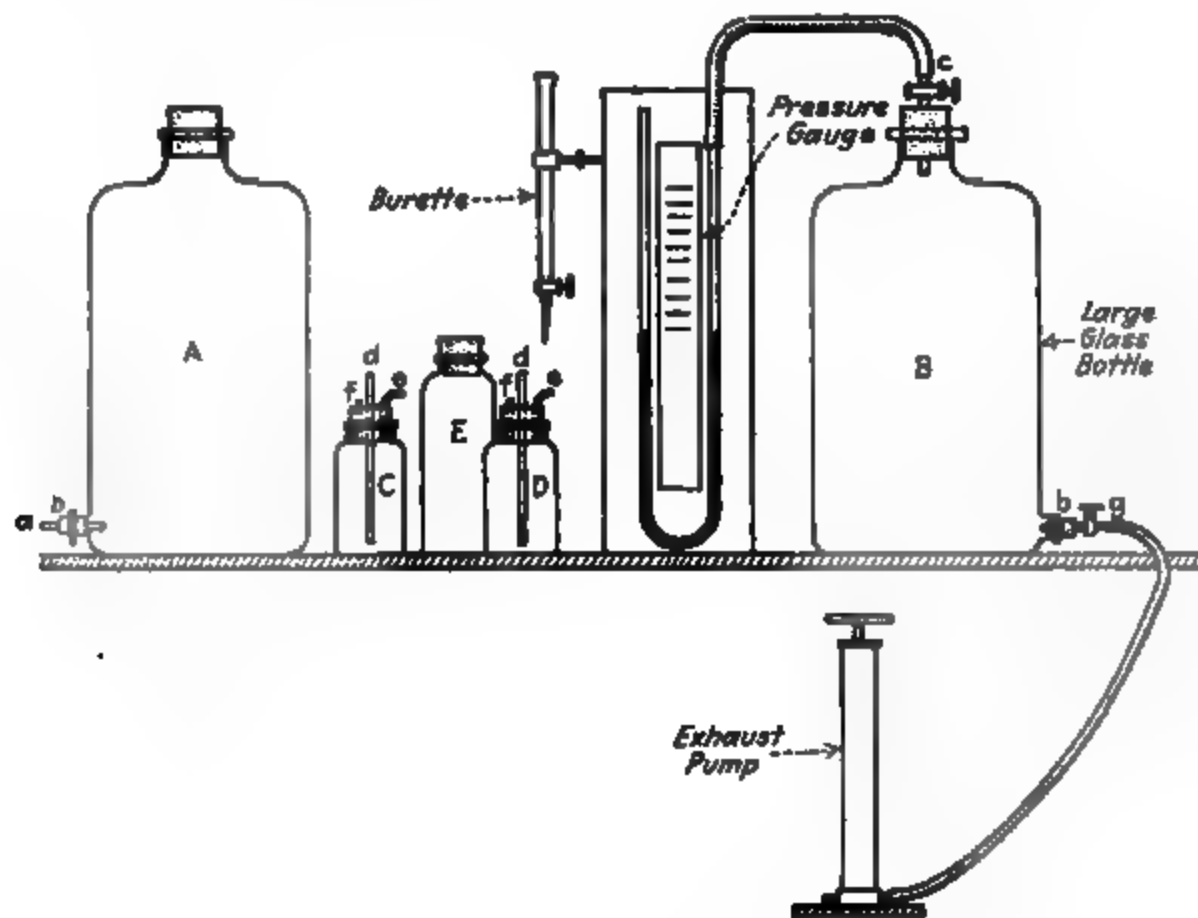


FIG. 137. Apparatus for Testing  $\text{SO}_2$  in Air.

Immediately before making a determination, a 300 to 400 cc. portion of starch solution in the mixing bottle is colored with iodine to a shade which experience indicates is suitable to the character of atmosphere to be analyzed and distributed in equal amounts to the aspirators in the same way as in the preliminary procedure. From this point to the operation of titration care is taken that both aspirators have the same exposure to sunlight.

The sample aspirator is now connected to the vacuum pump and gauge in the manner illustrated and evacuated to the extent determined by the conditions of strength of iodine solution, volume of aspirator bottle and temperature. Refer to formula on page 1284. For instance: Assuming that gas capacity of sample bottle is 19600 cc., the temperature to be 20° C. and that N/500 is the strength of the iodine solution, when the evacuation is carried close to 465 mm., each 0.05 cc. of the iodine solution required to bring the portion of starch iodide solution from the sample bottle to the same shade as that from the check bottle represents one tenth part per million of SO<sub>2</sub> by volume.

The sample is taken by letting the air in through the stopcock (c) while shaking the bottle so that its entire inner surface is kept wet with the starch iodide solution. When the internal pressure becomes that of the atmosphere the stopcock is closed and the bottle is shaken vigorously 60 to 80 times. The check bottle is shaken in the same manner, the same length of time and under the same condition of light.

The starch iodide solutions are returned to their corresponding titration bottles in the same manner as in the preliminary procedure, their colors compared and sufficient N/500 iodine solution added from the burette through the hole (f) to the solution from the sample bottle to make its shade that of the check.

Whenever it is evident that the color of the solution in the sample bottle is completely discharged, N/500 iodine is added through the hole (b) until the tint is near that of the check and the bottles again shaken for a minute. Several additions of iodine in this way may be required when the operator has misjudged the character of atmosphere. The solutions are finally compared in the titration bottles, the color intensity of the sample solution made that of the check and the SO<sub>2</sub> content of the sample calculated from the net amount of iodine added.

The operator may allow for a relatively high concentration of SO<sub>2</sub> in the sample by adding a noted quantity of iodine to the sample solution before its transfer to the aspirator bottle. In case the bleaching effect of the sample has not been sufficient to make the shade as light as that of the check solution, the SO<sub>2</sub> content can be calculated from the difference between the noted quantity of iodine added and that required to make the color of the check that of the sample solution.

It is apparent that each determination prepares the aspirator for the next provided that not a very long interval of time elapses between determinations. When a half hour or more has elapsed a trial should be made as in the preliminary procedure to determine whether the iodine consumption factor remains the same for both bottles.

The starch iodide solution can be used repeatedly but must be discarded as soon as it becomes in the least dirty.

**Beam test for suspended matter in gas.** See page 1502.

**Determination of suspended matter in gas.** See page 1502.

PROPERTIES OF DRY AIR  
Barometric Pressure 29.921 Inches

Tem- perature Degrees Fahr	Weight per Cu. Ft. Pounds	Per Cent. of Volume at 70° F.	B. t. u. Absorbed by One Cu. Ft. Dry Air per Degree F.	Cu. Ft. Dry Air Warmed One De- gree per B. t. u.	Tem- perature Degrees Fahr	Weight per Cu. Ft. Pounds	Per Cent. of Volume at 70° F.	B. t. u. Absorbed by One Cu. Ft. Dry Air per Degree F.	Cu. Ft. Dry Air Warmed One De- gree per B. t. u.
0	.08540	.8680	.02080	48.08	130	.06732	1.1133	.01631	61.32
5	.08544	.8772	.02060	48.55	135	.06675	1.1230	.01618	61.81
10	.08453	.8867	.02039	49.05	140	.06620	1.1320	.01603	62.31
15	.08363	.8962	.02018	49.56	145	.06565	1.1417	.01592	62.82
20	.08276	.9057	.01998	50.05	150	.06510	1.1512	.01578	63.37
25	.08190	.9152	.01977	50.58	160	.06400	1.1700	.01554	64.35
30	.08107	.9246	.01957	51.10	170	.06304	1.1890	.01530	65.36
35	.08025	.9340	.01938	51.60	180	.06205	1.2080	.01506	66.40
40	.07945	.9434	.01919	52.11	190	.06110	1.2270	.01484	67.40
45	.07866	.9530	.01900	52.64	200	.06018	1.2455	.01462	68.41
50	.07788	.9624	.01881	53.17	220	.05840	1.2833	.01419	70.48
55	.07713	.9718	.01863	53.68	240	.05673	1.3212	.01380	72.46
60	.07640	.9811	.01846	54.18	260	.05516	1.3590	.01343	74.46
65	.07567	.9905	.01829	54.68	280	.05367	1.3967	.01308	76.46
70	.07495	1.0000	.01812	55.19	300	.05225	1.4345	.01274	78.50
75	.07424	1.0095	.01795	55.72	350	.04900	1.5238	.01197	83.55
80	.07356	1.0190	.01779	56.21	400	.04618	1.6230	.01130	88.50
85	.07289	1.2083	.01763	56.72	450	.04364	1.7177	.01070	93.46
90	.07222	1.0380	.01747	57.25	500	.04138	1.8113	.01018	98.24
95	.07157	1.0472	.01732	57.74	550	.03932	1.9060	.00967	103.42
100	.07093	1.0570	.01716	58.28	600	.03746	2.0010	.00923	108.35
105	.07030	1.0660	.01702	58.76	700	.03423	2.1900	.00847	118.07
110	.06968	1.0756	.01687	59.28	800	.03151	2.3785	.00782	127.88
115	.06908	1.0850	.01673	59.78	900	.02920	2.5670	.00728	137.37
120	.06848	1.0945	.01659	60.28	1000	.02720	2.7560	.00680	147.07
125	.06790	1.1040	.01645	60.79	1200	.02392	3.1335	.00603	165.83

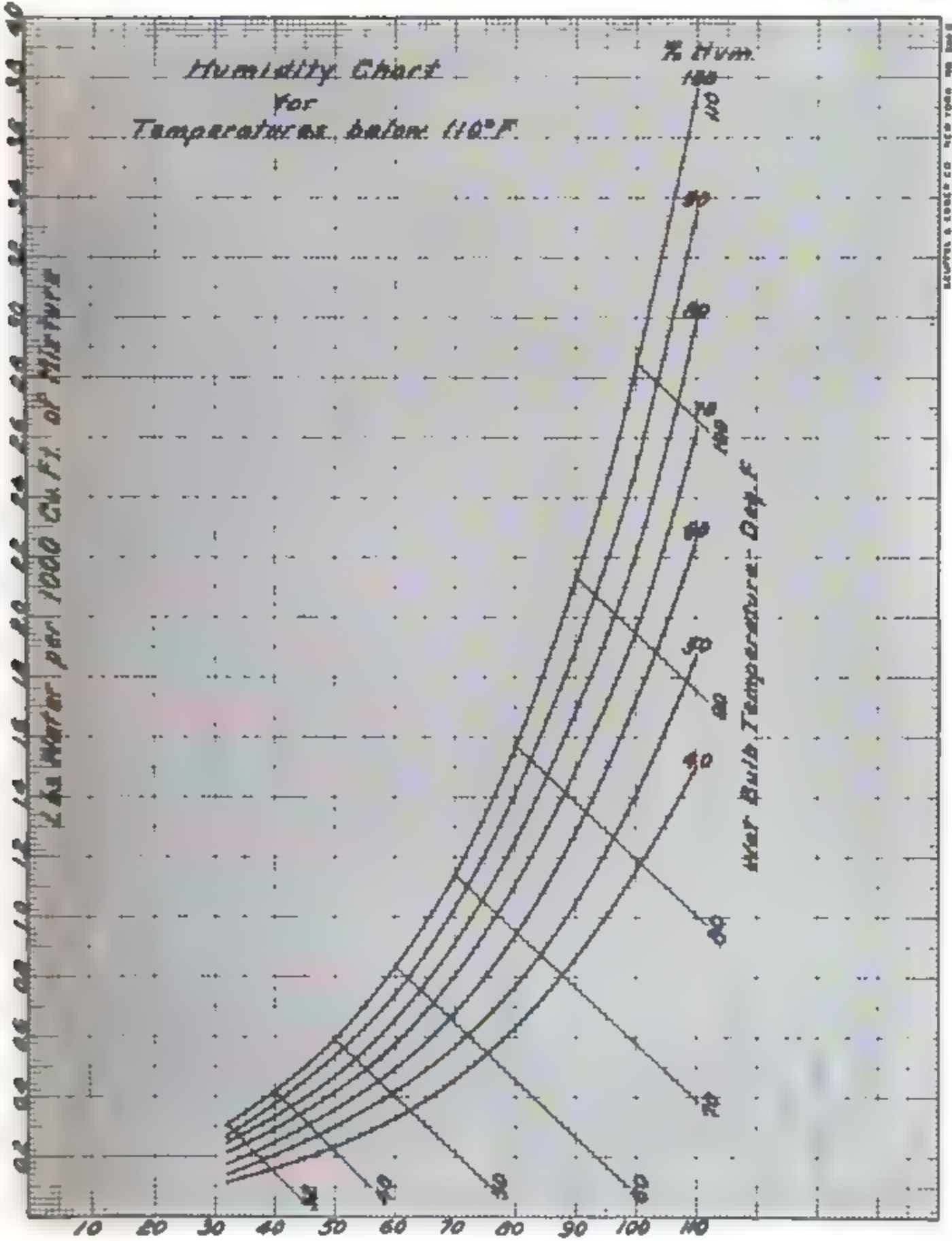
By courtesy of the Chemical Equipment Co.

## PROPERTIES OF SATURATED AIR

Weights of Air, Vapor of Water, and Saturated Mixture of Air and Vapor at Different Temperatures, Under Standard Atmospheric Pressure of 29.921 Inches of Mercury

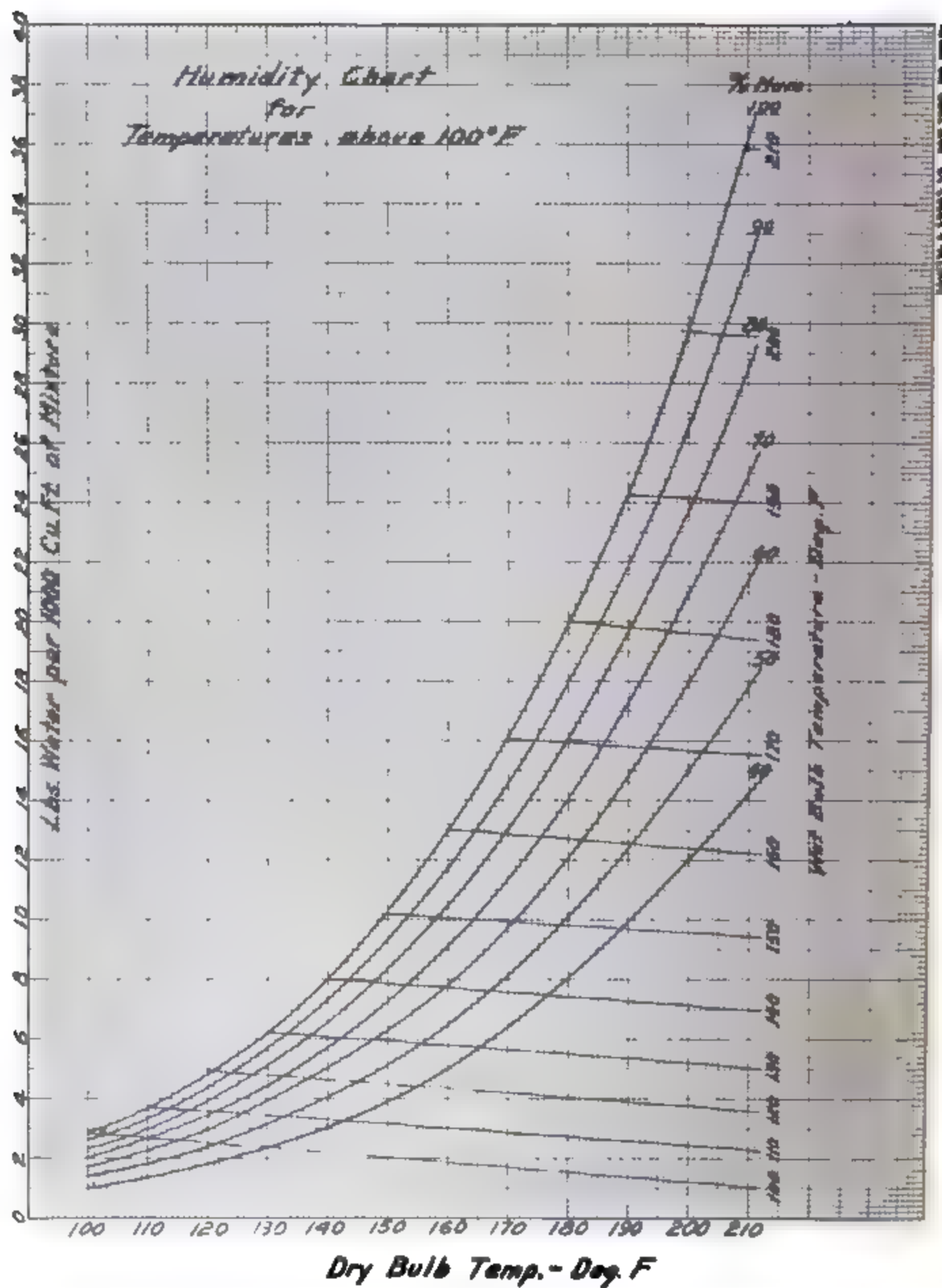
Temperature Degrees Fahr	Vapor Pressure Inches of Mer- cury	Weight in a Cubic Foot of Mixture			B. I. U. Ab- sorbed by One Cubic Foot Sat. Air. per Degree F.	Cubic Feet Sat. Air Warmed One Degree per B. I. U.
		Weight of the Dry Air Pounds	Weight of the Vapor Pounds	Total Weight of the Mixture Pounds		
1	2	3	4	5	6	7
0	.0383	.08625	.000069	.08632	.02082	48.04
10	.0631	.08433	.000111	.08444	.02039	49.05
20	.1030	.08247	.000177	.08265	.01998	50.05
30	.1640	.08063	.000276	.08091	.01955	51.15
40	.2477	.07880	.000409	.07921	.01921	52.06
50	.3625	.07694	.000587	.07753	.01883	53.11
60	.5220	.07506	.000829	.07589	.01852	54.00
70	.7390	.07310	.001152	.07425	.01811	55.22
80	1.0290	.07095	.001576	.07253	.01788	55.93
90	1.4170	.06881	.002132	.07094	.01763	56.72
100	1.9260	.06637	.002848	.06922	.01737	57.57
110	2.5890	.06367	.003763	.06743	.01716	58.27
120	3.4380	.06062	.004914	.06553	.01696	58.96
130	4.5200	.05716	.006357	.06352	.01681	59.50
140	5.8800	.05319	.008140	.06133	.01669	59.92
150	7.5700	.04864	.010310	.05894	.01663	60.14
160	9.6500	.04341	.012956	.05637	.01664	60.10
170	12.2000	.03735	.016140	.05349	.01671	59.85
180	15.2900	.03035	.019940	.05029	.01682	59.45
190	19.0200	.02227	.024465	.04674	.01706	58.80
200	23.4700	.01297	.029780	.04275	.01750	57.15

By courtesy of the Chemical Equipment Co.



**Dry Bulb Temp. - Deg. F**  
By courtesy of the Chemical Equipment Co.





By courtesy of the Chemical Equipment Co.

# EXAMINATION OF BITUMINOUS SUBSTANCES, INCLUDING ASPHALTS, TARS AND PITCHES

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The Ruberoid Co., N. Y.

## CLASSIFICATION OF BITUMINOUS SUBSTANCES

Table I contains a list of the principal commercial bituminous substances with a brief description of their origin or mode of production.

Although the methods included in this chapter are intended primarily for examining native asphalts, asphaltites, tars, pyrogenous asphalts and pitches, many of them may likewise be used for testing asphaltic pyrobitumens, native and pyrogenous waxes. Methods for examining petroleum are given in chapter on fixed oils, fats and waxes, and for testing non-asphaltic pyrobitumens (e.g., coal) in chapter on analysis of coal.

## CHEMICAL COMPOSITION OF BITUMINOUS SUBSTANCES

Bituminous substances are complex mixtures of saturated and unsaturated hydrocarbons, often associated with oxygenated, sulphurated and nitrogenous derivatives, and frequently admixed with mineral constituents in varying amounts.

The non-mineral constituents are accordingly composed of the elements carbon and hydrogen, with more or less oxygen, sulphur and nitrogen. It is a comparatively simple matter to ascertain by analytical methods the percentage by weight of the elements present. This is termed its *ultimate analysis*, in contra-distinction to the *molecular composition*.

The mineral constituents may be present in one or more of the following typical forms:

1. As consolidated mineral particles consisting of a porous rock impregnated with the bituminous constituents. This type is exemplified by the so-called "rock asphalts," which are usually composed of a fine-grained limestone or sandstone matrix, carrying the asphalt in its voids.

2. As unconsolidated mineral particles admixed mechanically with the bituminous constituents. This is typified by the numerous deposits of impure native asphalts and asphaltites, in which the bituminous constituents are associated with more or less detritus derived from the surrounding soil; also blast-furnace tar and pitch which carry a proportion of mineral dust carried over mechanically by the furnace gases.

3. As colloidal mineral particles held in suspension by the bituminous constituents. Trinidad Lake asphalt is typical of this group, and is characterized by the presence of colloidal clay and silica.

4. As mineral matter held in chemical combination by the non-mineral (i.e., pure bituminous) constituents. This group differs from the foregoing, inasmuch as it relates to a *chemical* union of the mineral and non-mineral components. Many native asphalts carry small percentages of iron and aluminum, but it is as yet a mooted question whether these are present as colloidal particles, or united chemically with the bituminous matter. Most residual and blown petroleum asphalts contain a trace of iron, derived from the stills in which they are refined.

## 1290 EXAMINATION OF BITUMINOUS SUBSTANCES

TABLE I.—BITUMINOUS SUBSTANCES

Genus	Species	Member	Remarks
Bitumens	Petroleums	Non-asphaltic petroleum.....	Contains an appreciable quantity of crystallizable paraffine and no asphalt.
		Mixed-base petroleum.....	Contains crystallizable paraffine, also asphalt.
		Asphaltic petroleum.....	Contains an appreciable quantity of asphalt and no crystallizable paraffine.
	Native mineral waxes	Ozokerite.....	A paraffinaceous mineral, called ceresine when refined.
		Montan wax.....	The wax extracted from lignite or pyropissite by means of solvents.
	Native asphalts	Pure or fairly pure....	Comparatively free from associated mineral matter (less than 10 per cent on the dry weight).
		Associated with mineral matter ("Rock Asphalt").....	Containing a substantial proportion of sand, sandstone, limestone, clay or shale.
	Asphaltites	Gilsonite.....	Extremely pure
		Glance pitch.....	Pure to moderately pure
		Grahamite.....	Pure to quite impure
Pyro-bitumens	Asphaltic pyrobitumens	Elaterite.....	Rubbery — partly saponifiable
		Wurtzilite.....	Depolymerizes on heating, becoming fusible and soluble
		Albertite.....	Depolymerizes partially on heating
		Imesonite.....	Does not depolymerize on heating
		Asphaltic pyrobituminous shales.....	Mineral matters predominate. Infusible and insoluble.
	Non-asphaltic pyrobitumens	Peat.....	Pure or fairly pure. Infusible and insoluble. Contain more or less oxygenated bodies. Derived from vegetable growths. Gradual transition from peat to lignite to coal.
		Lignite.....	
		Bituminous coal.....	
		Anthracite coal.....	
		Lignitic and coal shales.....	Mineral matters predominate, otherwise the same as the foregoing.

# EXAMINATION OF BITUMINOUS SUBSTANCES 1291

Genus	Species	Member	Remarks
Pyrogenous distillates	Pyrogenous waxes	Wax tailings. . . . .	Distillate from petroleum obtained immediately prior to coking.
		Petroleum paraffine. . .	Solid paraffine obtained from non-asphaltic petroleum.
		Peat paraffine. . . . .	Solid paraffine obtained from peat tar.
		Lignite paraffine. . . .	Solid paraffine obtained from lignite tar.
		Shale paraffine. . . . .	Solid paraffine obtained from shale tar.
	Tars	Oil-gas tar. . . . .	Produced by cracking petroleum vapors in manufacturing oil gas.
		Water-gas tar. . . . .	Produced by cracking petroleum vapors in manufacturing carburetted water gas.
		Pine tar. . . . .	Produced by the destructive distillation of the wood and roots of coniferae.
		Hardwood tar. . . . .	Produced by the destructive distillation of hardwoods.
		Peat tar. . . . .	Produced by the destructive distillation of peat.
		Lignite (brown coal) tar. . . . .	Produced by the destructive distillation of lignite brown coal.
		Shale tar. . . . .	Produced by the destructive distillation of pyrobituminous shales.
		Gas-works coal-tar. . . .	Produced from gas-house retorts in manufacturing gas from bituminous coal.
		Coke-oven coal-tar. . . .	Produced from by-product coke-oven in manufacturing coke from bituminous coal.
		Blast-furnace coal-tar. . .	Produced from blast-furnaces upon smelting metals with bituminous coal.
		Producer-gas coal-tar. . .	Produced from gas-producers in manufacturing producer gas from coal.
		Bone tar. . . . .	Produced by the destructive distillation of bones.
Pyrogenous residues	Pyrogenous asphalts	Residual oils. . . . .	Produced by the dry distillation of non-asphaltic petroleum, the dry or steam distillation of mixed-base petroleum, or the steam distillation of asphaltic petroleum.
		Blown petroleum asphalts. . . . .	Produced by blowing air through heated residual oils.
		Residual asphalts. . . . .	Produced by the steam distillation of mixed-base and asphaltic petroleum.

## 1292 EXAMINATION OF BITUMINOUS SUBSTANCES

Genus	Species	Member	Remarks
Pyrogenous residues	Pyrogenous asphalts	Sludge asphalts. .... Wurtzilite asphalt. . . .	Produced from the acid sludge obtained in the purification of petroleum distillates with sulphuric acid. Produced by depolymerizing wurtzilite in closed retorts.
	Pitches	Oil-gas-tar pitch. .... Water-gas-tar pitch. . . Wood-tar pitch. .... Peat-tar pitch. .... Lignite-tar pitch. .... Shale-tar pitch. .... Gas-works coal-tar pitch . . . . . Coke-oven coal-tar pitch . . . . . Blast-furnace coal-tar pitch . . . . . Producer-gas coal-tar pitch . . . . . Bone-tar pitch. .... Rosin pitch. ....  Fatty-acid pitch. ....	Residues obtained by the partial evaporation or distillation of the corresponding tars.  Residue obtained by the partial distillation of the resinous sap of coniferae. Residue obtained by the steam distillation of fatty-acids.

Fatty-acid pitch, wood-tar pitch, bone-tar pitch and rosin pitch carry a substantial amount of iron or copper depending upon whether they have been produced in an iron or copper still. Sludge asphalts bear a trace of combined lead derived from the lead containers in which they have been treated.

Native asphalts often contain non-mineral impurities in the form of decayed vegetable substances of peat-like nature, which were originally present in the soil, now associated with the asphalt. These substances are derivatives of humic, or ulmic, crenic, etc., acids.

Certain tars and pitches as well as residual asphalts which have been overheated in their process of manufacture, will carry variable amounts of so-called "free carbon." This in reality consists of hydrocarbon derivatives, polymerized under the influence of heat to an insoluble modification, similar in certain respects to bituminous coal. It is probable that the "free carbon" may under certain conditions consist in part of amorphous carbon, similar to lampblack.

Every member of the bituminous family is a homogeneous or heterogeneous mixture, consisting of a multitude of chemical substances, each having a definite molecular composition. These constituent substances may be associated as a simple solution of liquids in liquids or solids in liquids; or in the form of a colloidal solution; or as a solid solution of amorphous or crystalline solids; or as an emulsion of immiscible liquids; or as a suspension of insoluble substances in a more or less liquid matrix; or combinations of two or more of the foregoing phases.

At the present time but a comparatively small number of distinct chemical substances have been identified in bituminous complexes. A vast amount of research work must yet be accomplished. Although hundreds of non-mineral substances of definite molecular composition have been identified in petroleums, native mineral waxes, pyrogenous waxes and certain tars, comparatively little is known regarding the innumerable non-mineral molecular substances present in native asphalts, asphaltites, asphaltic pyrobitumens, non-asphaltic pyrobitumens, pyrogenous asphalts and pitches.

The chemistry of bituminous substances is further complicated by the fact that commercial specimens of any given material are rarely alike in composition. In some, certain chemical bodies predominate; in others, they may be present in smaller amounts; while in still others they may be absent. Thus two shipments of any given member of the bituminous family are apt to fluctuate widely in composition and physical properties, even when emanating from the same source. Again, a native bituminous substance derived from a single deposit will often vary, depending upon the degree of exposure and extent of metamorphosis. Native bituminous substances are in a constant state of transition, as the result of their age and environment. Pyrogenous bituminous substances show a marked variation in composition and physical properties, depending upon the raw materials used in their production and the exact conditions to which they have been subjected in their processes of manufacture, including the temperature, length of treatment, etc.

Bituminous substances should not therefore be compared to vegetable or animal fats or oils, which in the case of any given material will run fairly uniform in composition and physical properties.

In certain instances, comparatively simple tests have been devised for identifying single chemical bodies present, whereas in other cases the ultimate analysis of the material will furnish a clue to the identity of the substance under examination.

## PART I

EXAMINATION OF CRUDE, REFINED AND BLENDED  
BITUMINOUS SUBSTANCES

The methods ordinarily used for examining bituminous substances and their mixtures may be grouped under four headings, viz.:

- (1) Physical characteristics. (2) Heat tests.  
(3) Solubility tests. (4) Chemical methods of examination.

In general, these tests may have one or more of the following objects in view:

- (a) To serve as a means of identification.  
(b) To ascertain the value of the substance for a given purpose.  
(c) To gauge its uniformity of supply.  
(d) As an aid to factory control in its preparation, refining or blending.  
(e) As a criterion of its quality.

The most important methods of testing are given in Table II.

TABLE II

Description	For Purposes of Identification	Adaptability for a Given Purpose	Gauging the Uniformity of Supply	Purposes of Factory Control	As a Criterion of Quality
<i>Physical Characteristics:</i>					
Fracture.....	YES	....	....	....	....
Streak on Porcelain.....	YES	Yes	....	....	....
Specific gravity.....	YES	....	Yes	Yes	....
Viscosity.....	....	YES	Yes	Yes	....
Hardness or consistency.....	YES	YES	YES	YES	....
Susceptibility factor.....	YES	YES	YES	YES	....
Ductility.....	....	YES	Yes	Yes	....
<i>Heat Tests:</i>					
Fusing-point.....	YES	YES	YES	YES	....
Volatile matter.....	Yes	YES	Yes	Yes	....
Flash-point.....	....	YES	Yes	Yes	....
Fixed carbon.....	YES	....	....	....	....
Distillation test (for tars).....	Yes	YES	Yes	Yes	YES
<i>Solubility Tests:</i>					
Solubility in carbon disulphide....	YES	YES	YES	....	YES
Carbenes.....	Yes	....	Yes	Yes	YES
Solubility in 88° petroleum naphtha.....	YES	Yes	Yes	Yes	....
<i>Chemical Tests:</i>					
Water.....	Yes	....	....	....	YES
Carbon.....	YES	....	....	....	....
Hydrogen.....	YES	....	....	....	....
Sulphur.....	YES	....	....	....	....
Nitrogen.....	YES	....	....	....	....
Oxygen.....	YES	....	....	....	....
Free carbon in tars.....	YES	Yes	Yes	....	....
Solid paraffines.....	YES	....	....	....	....
Sulphonation residue.....	YES	....	....	....	....
Unsaponifiable matter.....	YES	....	Yes	....	YES
Diazo reaction.....	YES	....	....	....	....
Anthraquinone reaction.....	YES	....	....	....	....

<sup>1</sup> (a) Purity; (b) Care exercised in its preparation; (c) Intrinsic value.

**PHYSICAL CHARACTERISTICS****Fracture**

This is ascertained upon cleaving the specimen by subjecting it to a sharp blow, and examining the cleavage surface. Only hard and "brittle" bituminous substances will yield to this test, including the hard asphalts and asphaltites. The fracture may either appear conchoidal (rounded and curved like a shell), or hackly (jagged, irregularly and rough).

**Streak on Porcelain**

This represents the color of the powder which is left behind on drawing a piece of the solid bituminous material across the surface of unglazed porcelain. Hard bituminous materials only will yield to this test. The streak may be classified as white (where no streak is visible), yellowish, yellowish brown, brown, brownish black and black.

**Specific Gravity**

**Hydrometer Method for Fluid Materials.** Where speed is essential and great accuracy not required, the specific gravity of fluid bituminous materials may be determined with a hydrometer having its scale sub-divided to unity in the third place of decimals. (See also p. 1114.) Usually a series of hydrometers are used, ranging respectively from 0.800 to 0.900, 0.900 to 1.000, 1.000 to 1.080, 1.070 to 1.150, 1.150 to 1.230.

Most hydrometers are adapted to read at 60° F./60° F., or in other words, the instruments are calibrated for water at 60° F. taken as unity. The standard temperature for testing bituminous materials is 77° F., and they should accordingly be brought to this temperature when tested with the hydrometer. For correcting the reading to water at 77° F., it should be multiplied by 1.002, as follows:

$$\text{Sp.gr. at } 77^{\circ} \text{ F.} / 77^{\circ} \text{ F.} = \text{Sp.gr. at } 77^{\circ} \text{ F.} / 60^{\circ} \text{ F.} \times 1.002.$$

In running the test, the bituminous material is brought to 77° F., immediately poured into the hydrometer jar, and then the hydrometer slowly allowed to sink into it until it comes to a definite resting-point, whereupon it is raised slightly, and allowed to sink a second time. The reading is then noted. The hydrometer must not be pushed below the point at which it comes to rest until after the second reading has been taken, whereupon it should be pushed a slight distance below the end point to observe whether or not it will rise. If it fails to do so, it is evident that the bituminous material is too viscous to be tested by the hydrometer method, and some other method should be employed. Care should be taken that the hydrometer does not touch the sides or bottom of the cylinder when the reading is taken, also that the surface of the liquid is free from froth or bubbles.<sup>1</sup>

**Westphal Balance Method.** This is also adapted to testing fluid bituminous materials. The instrument as supplied by the manufacturer (see p. 1111) is provided with a cylinder of about 50 cc. capacity, calibrated for use at 60°/60° F. The test generally made at 77° F., is subject to the same correction as in the hydrometer method.

The Westphal balance may be adapted for as little as 8 cc. of the bituminous material, by using a special plummet, small enough to fit into a 10 cc. cylinder. The plummet may be made from a piece of glass tubing 7 mm. outside diameter, which is sealed at one end with a short platinum wire fused into the glass. Nine to ten grams of mercury are placed in the tube forming a column 35-40 mm. high. The tube is then cut off within 20 mm. of the top of the mercury column, and the open end sealed with a blow-pipe. This plummet should measure 55-60 mm. over all, and weigh from 10 to 12 g. If *a* represents the weight of the plummet in air, *b* its weight in water at a definite temperature, and *c* its weight in the bituminous material at the same temperature,

then the specific gravity of the bituminous material at this temperature =  $\frac{c-a}{b-a}$ .<sup>2</sup>

<sup>1</sup> Bulletin No. 314, U. S. Dept. of Agr., Wash., D. C., Dec. 10, 1915; "Laboratory Manual of Bituminous Materials," by Prevost Hubbard, p. 30, N. Y., 1916; "Specific Gravity—its Determination for Tars, Oils and Pitches," by J. M. Weiss, J. Ind. Eng. Chem., 7, 21, 1915.

<sup>2</sup> "Standard Methods for Sampling and Analysis of Creosote Oil" (Serial Designation: D 38-18) of the Am. Soc. Testing Materials, Standards Adopted in 1918, 731.



## 1296 EXAMINATION OF BITUMINOUS SUBSTANCES

**Pycnometer or Specific-Gravity Bottle Method.** Several forms of glass bottles are used for this purpose, having a ground-glass stopper with a small vertical hole bored through, to enable it to be completely filled with the bituminous material. These are made in various sizes.

An improvised form which may be used to good advantage when a small quantity of liquid bituminous material is available, consists of a 1 cc. pipette, and a glass tube sealed at one end, the inside diameter of which is slightly larger than the outside diameter of the lower stem of the pipette. On using this instrument, the liquid is first brought to a definite temperature, then sucked to the upper mark of the pipette by means of a piece of rubber tubing temporarily attached to its upper stem. The outside is carefully wiped dry and the lower stem inserted in the glass tube which serves to retain any liquid which may drain from the pipette. A small piece of wire twisted about the pipette near the top is formed into a ring to hang it from the hook above a balance pan. The pipette is thus supported in a vertical position and weighed.<sup>1</sup>

If  $a$  represents the weight of the pipette with glass tube empty,  $b$  its weight filled with water at a definite temperature, and  $c$  its weight filled with the bituminous material at the same temperature, then the specific gravity may be calculated from the following formula:

$$(c-a) \div (b-a).$$

It is customary to determine the specific gravity of bituminous materials at 77°/77° F., although in the case of creosote oil it is often expressed at 100°/60° F. For converting the specific gravity of a substance found at a higher temperature to the standard temperature (lower), the following formula should be used:

$$\text{Sp.gr. Substance at } t_1/t_1 = \text{Sp.gr. Substance at } t_2/t_1 + k(t_2 - t_1),$$

in which  $t_2$  = the temperature at which the specific gravity of the substance was determined,

$t_1$  = the temperature (lower) at which the specific gravity of the substance is to be calculated, and

$k$  = the coefficient of expansion, which is constant for the particular substance.

If perchance the specific gravity of the substance has been compared with that of water at a higher temperature, then to convert it to a lower temperature compared with water at the same temperature, the following formula should be used:<sup>2</sup>

$$\text{Sp.gr. Substance at } t_1/t_1 = \text{Sp.gr. Substance at } t_2/t_2 \times \text{Sp.gr. Water at } t_2/t_1 + k(t_2 - t_1).$$

In both of the above formulae, the following values may be taken approximately for  $k$ , representing the coefficient of expansion per ° F.

Creosote oil from coal tar . . . . .	0.00044
Residual oil . . . . .	0.00040
Coal tar . . . . .	0.00038
Coke-oven tar . . . . .	0.00033
Semi-solid asphalt . . . . .	0.00030
Semi-solid coal-tar pitch . . . . .	0.00030

The pycnometer method may also be used for finding the specific gravity of hard and brittle bituminous substances, including hard asphalts of high fusing-point, asphaltites, asphaltic pyrobitumens, non-asphaltic pyrobitumens and pyrobituminous shales. Approximately 3.5 grams of the material ground to 60-mesh are carefully weighed and introduced into a 50-cc. pycnometer, with about 30 cc. of distilled water. A vertical condensing bulb is attached to the pycnometer with a small section of rubber tubing, the open end being connected with an aspirator to maintain a partial vacuum. The pycnometer is then boiled on a water bath to expel all the air from the sample. The inside of the condensing tube is then washed back into the pycnometer, which is cooled to the desired temperature, stoppered, filled to the mark with water at the same temperature and weighed. The specific gravity may then be calculated from the following formula:

$$(c-a) \div [(b-a) - (d-c)].$$

Where  $a$  represents the weight of the pycnometer empty,  $b$  its weight filled with water,  $c$  its weight containing the bituminous substance, and  $d$  its weight containing the bituminous substance also filled to the mark with water.

In the case of fusible semi-solid or solid bituminous materials, the dry pycnometer is filled half full with the melted substance, cooled to 77° F., then weighed, then filled with water at 77° F. to the mark and reweighed. The specific gravity is calculated by means of the foregoing formula.

<sup>1</sup> "Specific Gravity—Its Determination for Tars, Oils and Pitches," by J. M. Weiss, loc. cit.

<sup>2</sup> For the specific gravity of water at varying temperatures, see Bureau of Standards, Circular No. 19, p. 43, Mar. 30, 1916.

## Viscosity

**Engler Method.** The method as described on p. 1114 is adapted for examining liquid to semi-liquid bituminous substances, which are generally tested at 77° F. (25° C.), 172° F. (50° C.), or 212° F. (100° C.) depending upon their consistency.

**Float Test.** This instrument is used largely for testing the viscosity or consistency of semi-solid bituminous materials. The range of the float test is limited, and it cannot be used with very fluid bituminous materials or with hard solids. It accordingly fills the gap between the Engler viscosimeter on one hand, and the needle penetrometer and consistometer on the other. The test is not affected by the presence of finely-divided mineral matter or free carbon.

The instrument is illustrated in Fig. 138. It consists of two parts, viz.: an aluminium saucer-shaped float and a conical brass collar weighing together exactly 50 g.

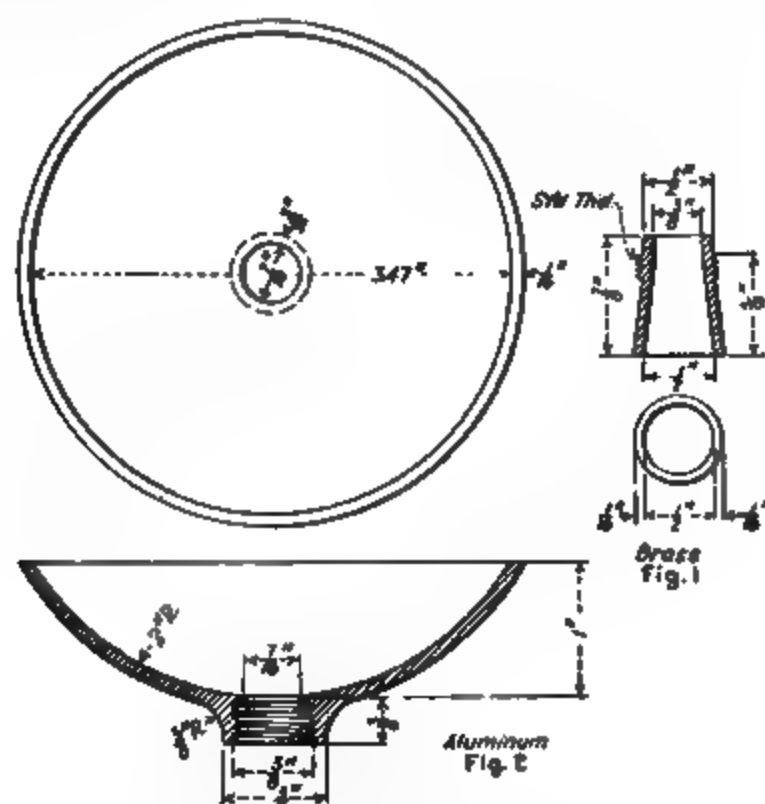


FIG. 138.—Float Tester.

The brass collar is filled with melted bituminous material upon placing it against a brass plate, the surface of which has been amalgamated by treatment with a dilute solution of mercuric chloride and then with mercury. After cooling, it is levelled, placed in water at 41° F. for 15–30 minutes along with the aluminium float, then screwed into the float and immediately floated with the brass collar downward on the surface of water warmed to the desired temperature. No standard temperature has been adopted for making this test, although 90° F. is recommended as most satisfactory in testing road binders, for which the instrument is intended. Very soft materials are tested at 32° F., and harder bituminous substances at 122° F. or 150° F.

As the heat is transmitted through the brass collar into the plug of bituminous material, the latter softens until it is forced upward and out of the collar by the weight of the instrument. The time elapsing between the placing of the float on the surface of the water, and when the water breaks through the plug is taken as a measure of the viscosity of the material under examination.<sup>1</sup>

<sup>1</sup> "Controlling the Consistency of Bituminous Binders," by C. N. Forrest, Eng. Rec., 50, 584, 1909; J. Ind. Eng. Chem., 1, 378, 1909; "Standard Methods for Sampling and Analysis of Creosote Oil" (Serial Designation: D 38-18) A. S. T. M. Standards, Adopted in 1918, 732.

## Hardness or Consistency

**Needle Penetrometer.** This was originally devised by H. C. Bowen in 1888.<sup>1</sup> This first crude instrument was further improved by A. W. Dow.<sup>2</sup> The Dow penetrometer as simplified in construction by Richardson and Forrest represents the type in use to-day,<sup>3</sup> both forms operating on the same principle and giving the same readings.

The Richardson-Forrest improved penetrometer is illustrated in Fig. 139. The base *A* may be levelled by the thumb screws *B*, and is attached to the standard *C* and also the platen *D*, which by means of a screw-shank raises or lowers the revolving disc *E*, on which is placed the sample of bituminous material to be tested. The standard *C* carries a bracket *F* adjustable as to elevation by a thumb-screw, also the bracket *G*, which on the back carries the clock-work *H* timing the duration of the test by half-second beats, and on the front the dial *J* divided into 360 degrees, with the hand *K*, marking the number of degrees, each of which represents one-tenth millimeter of penetration measured by rack on sliding gauge *L*, engaging in pinion on the shaft which actuates the hand *K*. The bevelled-edge mirror *N* adjustable through universal joints, serves to reflect light on the sample under test. The plunger *O* acts as a brake, which holds the needle bar, representing a weight of 50 g. together with the superincumbent weight in place, until pressed inward, which movement permits the needle and weight to act upon test-block without friction, and is easily operated by grasping the horns *Q* between two fingers and pressing the brake-head *O* with the thumb. *M* represents a weight of predetermined capacity, either 50 or 150 g. A form of penetrometer operated by an electrical timing device has also been constructed.<sup>4</sup> A miniature penetrometer for portable use is illustrated in Fig. 140.

Careful investigations have been made as to the diameter of the holder for the bituminous material;<sup>5</sup> the method of preparing the specimen;<sup>6</sup> the size and shape of the needle;<sup>7</sup> also other variable factors.<sup>8</sup> As a result of these, the following standard test has been adopted.<sup>9</sup>

<sup>1</sup> S. of M. Quarterly, 10, 297, 1889; U. S. Pat. 404,974 of Apr. 4, 1893 to H. C. Bowen; "Report of the Operations of the Engineer Department of the District of Columbia," p. 106, for 1889-90; also article by Clifford Richardson in Eng. Record of Oct. 31, 1891.

<sup>2</sup> "Report of the Engineer Dept. of the District of Columbia, for year ending June 30, 1898," p. 127, "Report of the Inspector of Asphalt and Cement of the District of Columbia for the year ending June 30, 1901," p. 158, by A. W. Dow; "Testing of Bitumens for Paving Purposes," by A. W. Dow, Proc. Am. Soc. Testing Materials, 3, 354, 1903; "Relation between Some Physical Properties of Bitumens and Oils," by A. W. Dow, Proc. Am. Soc. Testing Materials, 6, 497, 1906.

<sup>3</sup> "The Development of the Penetrometer as Used in the Determination of the Consistency of Semi-Solid Bitumens," by Clifford Richardson and C. N. Forrest, Proc. Am. Soc. Testing Materials, 7, 626, 1907; "A Further Development of the Penetrometer as Used in the Determination of the Consistency of Semi-Solid Bitumens," by C. N. Forrest, Proc. Am. Soc. Testing Materials, 9, 600, 1909.

<sup>4</sup> U. S. Pat. 512,687 of Jan. 16, 1894 to A. W. Dow and T. R. Griffith; H. W. Mahr, J. Ind. Eng. Chem., 6, 133, 1914.

<sup>5</sup> "Effect of Diameter of Bitumen Holder on the Penetration Test," by C. S. Reeve, Proc. Int. Assoc. Testing Materials, Sixth Congress, N. Y., XXV-3, 1912.

<sup>6</sup> Proc. Am. Soc. Testing Materials, 16, Part I, 306, 1916; "Revised Standard Test for Penetration of Bituminous Materials," by L. W. Page, Chem. Eng. Manuf., 24, 32, 1916.

<sup>7</sup> "A New Penetration Needle for Use in Testing Bituminous Materials," by C. S. Reeve and F. P. Pritchard, J. Agric. Research, 5, 1121, 1916.

<sup>8</sup> "Effect of Controllable Variables on the Penetration Test for Asphalts and Asphalt Cements," by Prévost Hubbard and F. P. Pritchard, J. Agric. Research, 5, 805, 1916.

<sup>9</sup> "Standard Test for Penetration of Bituminous Materials" (Serial Designation: D 5-16), A. S. T. M. Standards Adopted in 1916, 530; A. S. T. M. Standards 1918, 632.

"Penetration is defined as the consistency of a bituminous material, expressed as the distance that a standard needle vertically penetrates a sample of the material under known conditions of loading, time and temperature. Where the conditions of test are not specifically mentioned, the load, time and temperature are understood to be 100 g., 5 seconds and 77° F. respectively, and the units of penetration to indicate hundredths of a centimeter.



Courtesy of Howard & Morse.  
FIG. 139.—Penetrometer.



Courtesy of Howard & Morse.  
FIG. 140.—Miniature Penetrometer.



"The container for holding the material to be tested shall be a flat-bottom cylindrical dish, 55 mm. ( $2\frac{1}{4}$  in.) in diameter and 35 mm. ( $1\frac{1}{2}$  in.) deep. The needle for this test shall be a cylindrical steel rod 50.8 mm. (2 in.) long, having a diameter of 1.016 mm. (0.04 in.) and turned on one end to a sharp point having a taper of 6.35 mm. ( $\frac{1}{4}$  in.). The water bath shall be maintained at a temperature not varying more than 0.2° F. from 77° F. The volume of water shall not be less than 10 litres, and the sample shall be immersed to a depth of not less than 10 cm. (4 in.) and shall be supported on a perforated shelf of not less than 5 cm. (2 in.) from the bottom of the bath. Any apparatus which will allow the needle to penetrate without appreciable friction and which is accurately calibrated to yield results in accordance with the definition of penetration, will be acceptable. The transfer-dish for container shall be a small dish or tray of such capacity as will insure complete immersion of the container during the test. It shall be provided with some means which will insure a firm bearing and prevent rocking of the container.

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The sample shall be completely melted at the lowest possible temperature and stirred thoroughly until it is homogeneous and free from air bubbles. It shall then be poured into the sample container to a depth of not less than 15 mm. ( $\frac{1}{2}$  in.). The sample shall be protected from dust and allowed to cool in an atmosphere not lower than 65° F. for 1 hour. It shall then be placed in the water bath along with the transfer dish and allowed to remain 1 hour.

"In making the test, the sample shall be placed in the transfer dish, filled with water from the water bath of sufficient depth to completely cover the container. The transfer dish containing the sample shall then be placed upon the stand of the penetration machine. The needle, loaded with specified weight, shall be adjusted to make contact with the surface of the sample. This may be accomplished by making contact of the actual needle-point with the image reflected by the surface of the sample from a properly placed source of light. Either the reading of the dial shall then be noted, or the needle brought to zero. The needle is then released for the specified period of time, after which the penetration machine is adjusted to measure the distance penetrated.

"At least three tests shall be made at points on the surface of the sample not less than 1 cm. ( $\frac{1}{2}$  in.) from the side of the container, and not less than 1 cm. ( $\frac{1}{2}$  in.) apart. After each test the sample and transfer dish shall be returned to the water bath and the needle shall be carefully wiped toward its point with a clean dry cloth to remove all adhering bituminous matter. The reported penetration shall be the average of at least three tests whose values shall not differ more than 4 points between maximum and minimum. When desirable to vary the temperature, time and weight, and to provide for uniform method of reporting results when such variations are made, the samples shall be melted and cooled in air as above directed. They shall then be immersed in water or brine, as the case may require, for 1 hour at the temperature desired. The following combinations are suggested:

32° F.; 200 g. weight; 60 seconds,  
77° F.; 100 g. weight; 5 seconds,<sup>1</sup>  
115° F.; 50 g. weight; 5 seconds."

**Consistometer.** This instrument is constructed according to scientific principles, and may accurately be duplicated at any time. It registers the degrees hardness on a scale ranging from 0 to 100, and is suitable for determining the hardness of substances as soft as vaseline (which will test 0.3 at 77° F.) to substances as hard as gilsonite (testing in the neighborhood of 100 at 77° F.). In all cases, the hardness or consistency is expressed as the cube root of the number of grams which must be applied to a circular flat surface 1 sq. cm. (100 sq. mm.) in area, to cause it to displace the substance at a speed of 1 cm. per minute. Readings for all bituminous substances and at all temperatures (whether 115, 77 or 32° F.) are expressed on a *single* scale. The harder the substance, the greater will be its hardness expressed numerically.

Four mushroom-shaped plungers are used, each having a round flat head with a reduced shank, so the perimeter of the penetrating surface forms a "knife" edge. This entirely eliminates the fractional adhesion of the bituminous substance to the sides of the plungers. The flat heads of the plungers are made in the following dimensions:

Plunger	Diameter in Mm.	Area in Sq. Mm.
No. 1 . . . . .	1.13	1
No. 10 . . . . .	3.57	10
No. 100 . . . . .	11.28	100
No. 1000 . . . . .	35.67	1000

The method of testing consists in forcing one of the plungers into the substance at a uniform speed of 1 cm. per minute. The force is automatically registered in grams or kilograms. For any plastic substance, the number of grams required to effect this displacement is directly proportional to the volume displaced. The volumes displaced per minute by the respective plungers are 0.1, 0.10, 1.00 and 10.0 cc. respectively. The relation between the plungers is therefore in the direct proportion of 1 : 10 : 100 : 1000.

<sup>1</sup> Inserted by author. Not included in the printed method published by the Am. Soc. Testing Materials.

Two interchangeable springs are supplied, one registering in grams on a scale ranging 0 to 1000 g., in 10 g. divisions, and the other for reading in kilograms on a scale ranging from 0 to 10 kgs., in 0.1 kg. divisions. In using plungers No. 1 and No. 10, the kilogram spring only should be employed. In using plunger No. 100 either the gram or the kilogram spring may be employed, depending upon the hardness of the material. In using plunger No. 1000, the gram spring *only* should be employed. The relations are expressed in the following table:

Plunger	Spring	Actual Reading	Converted to Grams per 100 Sq. Mm. Plunger	Cube Root Grams Applied 100 Sq. Mm. Plunger
1000 sq.mm.....	G.	{ From 10 g. to 1000 g.	1 100	1.00 4.64
100 sq.mm.....	{ G. Kg.	{ From 100 g. to 1000 g. From 1.0 kgs. to 10.0 kgs.	100 1,000 1,000 10,000	4.64 10.00 10.0 21.5
10 sq.mm... ..	Kg.	{ From 1.0 kg. to 10.0 kgs.	10,000 100,000	21.5 46.4
1 sq.mm.....	Kg.	{ From 1.0 kg. to 10.0 kgs.	100,000 1,000,000	46.4 100.0

The consistometer is illustrated in Fig. 141. It is first levelled by the four screws *A*. The spring *B* is then attached, selecting the gram spring for soft substances, or the kilogram spring for hard substances. The steel shaft *C* is inserted and screwed firmly into place. The plunger *D* should then be screwed into the lower end of the shaft. Plunger No. 1 is used for hard and brittle substances, plunger No. 10 for moderately hard solid substances, plunger No. 100 for moderately soft semi-solid substances, and plunger No. 1000 for semi-liquid substances.

The scale *E* is graduated in grams on one side, and kilograms on the other, and is reversible. It should be inserted so that the graduations will correspond with the spring used, and adjusted so the indicator *F* will rest at the 0 division. The maximum indicator *G* is also brought to the 0 division using the small instrument *H*.

The bituminous substance is melted at the lowest possible temperature and poured into a small receptacle as described for the needle penetration method. The tin box *J* containing the bituminous substance is then supported underneath the machine in a vessel of water (not shown) maintained at the temperature at which the test is to be performed. The pressure is applied to the plunger by turning the hand-wheel *O*, and the speed of displacement controlled by following the pointer *K*, on the dial *L*, which should be caused to revolve at the same speed as the second hand of a chronometer *M*, conveniently suspended alongside. The numbers on the dial *L* correspond with those of the second hand on the chronometer. One revolution of the pointer *K* indicates that the plunger has moved downward exactly one centimeter.

At the termination of 60 seconds, after the pointer on the dial has made one revolution, the pressure on the plunger is relieved. The reading of the maximum indicator *G* on the scale *E* is then noted, and the corresponding degree of hardness ascertained by referring to the table supplied with the instrument.

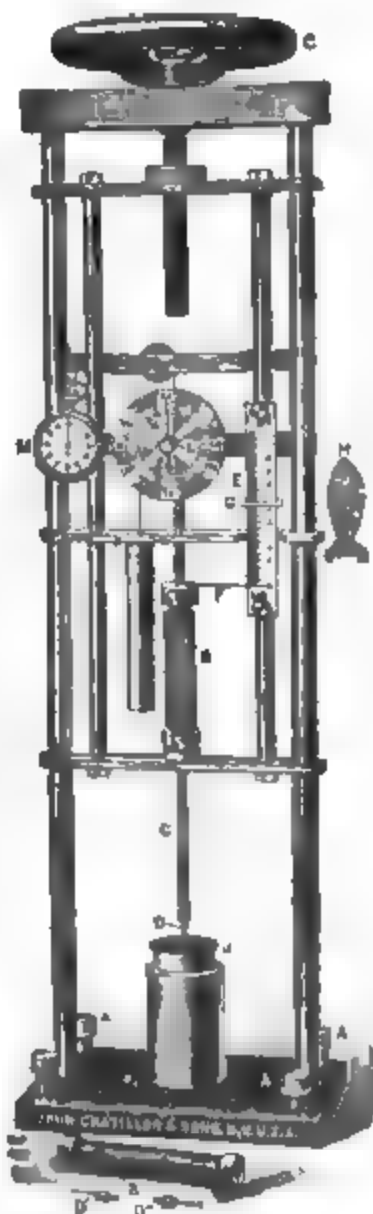


FIG. 141—Consistometer.

## 1302 EXAMINATION OF BITUMINOUS SUBSTANCES

When the plunger commences to displace the substance at the specified speed of 1 cm. per minute, a maximum reading is obtained which should remain constant throughout the entire displacement. The consistometer is simple to operate, gives closely concordant results, expresses the readings obtained at all temperatures on *one scale* and has a sufficiently great range to include all bituminous substances ordinarily encountered.<sup>1</sup>

**Susceptibility Factor.** This factor is a numerical expression representing the susceptibility of a bituminous substance to temperature changes. The more susceptible the material the higher will be its "susceptibility factor." It is calculated from the consistometer hardness and the K. and S. fusing-point in the following manner:

$$\text{Susceptibility Factor} = \frac{(\text{Hd at } 32^{\circ} \text{ F.}) - (\text{Hd at } 115^{\circ} \text{ F.})}{\text{Fusing-point, K. and S. Method}} \times 100$$

By means of the susceptibility factor, bituminous materials may be roughly divided into the following groups, viz.:

*Susceptibility Factor under 40:* Includes blown petroleum asphalts, fatty-acid pitches and fluxed asphaltites (having a factor between 8 and 40); also wurtzilite asphalts (having a factor between 30 and 40).

*Susceptibility Factor between 40 and 60:* Includes residual asphalts.

*Susceptibility Factor over 60:* Includes mineral waxes, pitches derived from tars, and asphaltites (of which the susceptibility factor varies from 75 to over 100).

Native asphalts have been excluded from the foregoing groups, since their susceptibility factors vary widely, ranging from 15 to greater than 100. The author has never examined a bituminous material having a susceptibility factor lower than 8.<sup>2</sup>

### Ductility

This represents the capacity of the bituminous material for elongating or stretching.

There are two methods in use, depending upon the construction of the moulds, namely one devised by A. W. Dow, and one proposed by the author.

**Dow Ductility Test.** The Dow mould is constructed of four brass parts as illustrated in Fig. 142, and of the following dimensions: external length 9 cm., internal



Courtesy of Humboldt Mfg. Co.

FIG. 142.—Dow Ductility Mould.

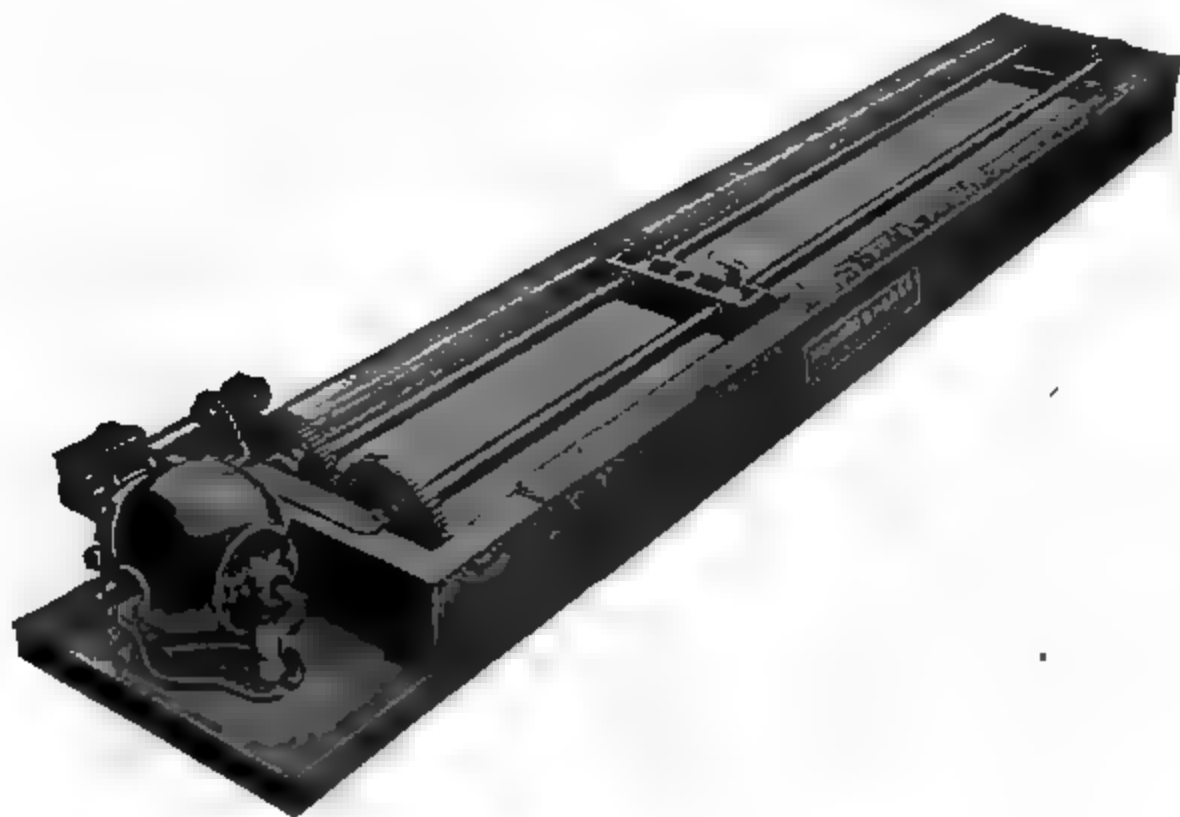
length 7.5 cm., distance between the ends of clips 3.0 cm., extreme internal width of mould 3.0 cm., internal width at mouth of clips 2.0 cm., internal cross-section half-way between clips 1.0 cm., and thickness of briquette 1.0 cm.<sup>3</sup> The two centre pieces should

<sup>1</sup> "Improved Instruments for the Physical Testing of Bituminous Materials," by Herbert Abraham, Proc. Am. Soc. Testing Materials, 9, 568, 1909; 11, 676, 1911; U. S. Pat. 989,471 of Apr. 11, 1911 to Herbert Abraham.

<sup>2</sup> "Improved Instruments for the Physical Testing of Bituminous Materials," by Herbert Abraham, Proc. Am. Soc. Testing Materials, 11, 683, 1911.

<sup>3</sup> "The Testing of Bitumens for Paving Purposes," by A. W. Dow, Proc. Am. Soc. Testing Materials, 3, 352, 1903; "Report of the Commissioners of the Dist. of Columbia, for the year ending June 30, 1904," p. 42; "Methods for Testing Asphalt," by A. W. Dow, Chem. Eng., 1, 330, 1905; "Tests of Asphalts for Paving Purposes," by A. W. Dow and F. P. Smith, Munic. Eng., 40, 437, 1911.

be well amalgamated to prevent the bituminous material from adhering, and the mould assembled on an amalgamated brass plate. The bituminous material is melted at the lowest possible temperature, poured in a steady stream into the center of the mould, and a slight excess added to allow for shrinkage on cooling. The mould is cooled in air and levelled off with a hot spatula. The center pieces are then removed, leaving the briquette of bituminous material held at either end by the clips, and carefully transferred to a vessel of water maintained within 1 degree of the required temperature for at least 1, but not longer than 2 hours. The clips should then be pulled apart under water maintained within 1 degree of the required temperature, at a uniform rate of speed of 5 cm. per minute. The line of pull should be horizontal or nearly so, and the separation effected without appreciable vibration. Three tests should be averaged.<sup>1</sup> It is custom-



Courtesy of Howard & Morse.

FIG. 143.—Smith Ductility Machine.

ary to make this test at three temperatures, viz.: 115, 77 and 32° F. Various machines have been proposed for this purpose, including the one devised by Smith, illustrated in Fig. 143.<sup>2</sup>

<sup>1</sup> "Report of Sub-Committee on Ductility Tests," Proc. Am. Soc. Testing Materials, Part I, 15, 349, 1915.

<sup>2</sup> "Machine for Testing the Ductility of Bituminous Paving Cements," by F. P. Smith, Proc. Am. Soc. Testing Materials, 9, 594, 1909.



## 1304 EXAMINATION OF BITUMINOUS SUBSTANCES

**Abraham's Ductility Test.** An improved mould designed by the author, is illustrated in Fig. 144 and shown in cross-section in Fig. 145. It consists of two cylindrical sections

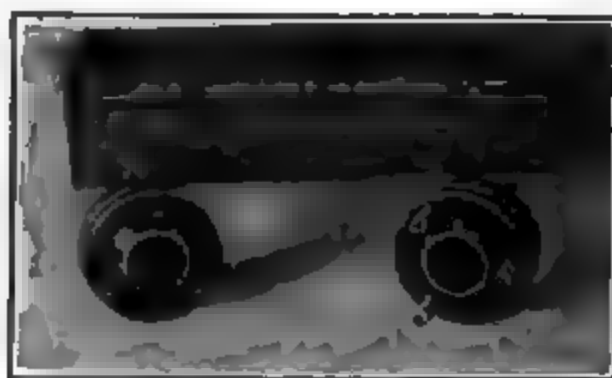


FIG. 144.—Abraham's Ductility Mould.

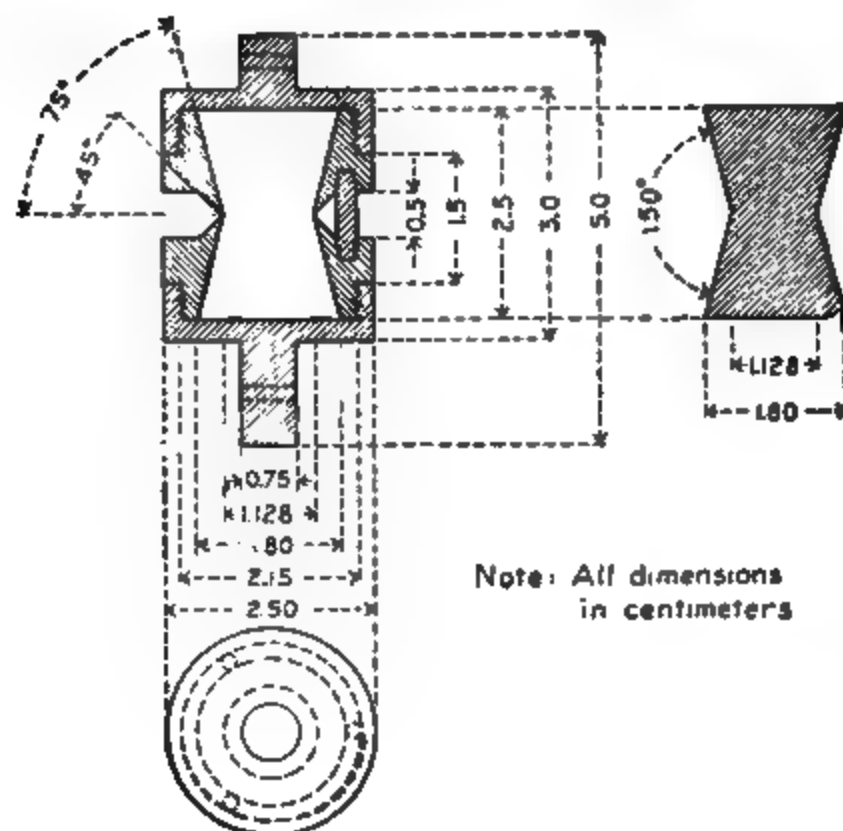


FIG. 145.—Cross-section Abraham's Mould.

constructed of hardened steel, resting together on circular knife-edges and maintained in that position by three guide pins. It is filled by unscrewing the upper cap and pouring in the melted bituminous substance, which on cooling forms a prismoid, whose altitude is 2.5 cm., the end-areas 1.8 cm. in diameter, with a minimum cross-section at the center of exactly 1.0 sq.cm. (1.28 cm. in diameter). The upper cap is screwed in place, the mould fastened in the tensometer and the two halves separated at the uniform speed of 5 cm. per minute. The elongation in cms. at the moment the material parts is a measure of its ductility.<sup>1</sup>

This mould has a number of advantages over the Dow type, including its adaptability to testing semi-liquid and semi-solid bituminous materials, no amalgamation is necessary, there is no danger of the material breaking in the mould upon being cooled to the proper temperature, the personal equation is eliminated in filling the mould with the assurance that the minimum cross-section will be *exactly* the proper size, and only a small quantity of the material is required in making the test.

<sup>1</sup> "Improved Instruments for the Physical Testing of Bituminous Materials," by Herbert Abraham, *Proc. Am. Soc. Testing Materials*, 10, 444, 1910; 11, 679, 1911.

## HEAT TESTS

Fusing ("Softening") Point<sup>1</sup>

This constitutes one of the most valuable all-around tests. Several methods have been proposed for this purpose, viz.:

**Kramer-Sarnow Method.** This method is rapid, accurate, and adapts itself either to soft or hard bituminous materials, from residual oils up to grahamite. Its range is greater than that of any other fusing-point method.

It was first proposed by G. Kramer and C. Sarnow.<sup>2</sup> Various modifications have been suggested from time to time.<sup>3</sup> The author has made a careful study of this method, and recommends the following procedure:<sup>4</sup>

**Substances Fusing below 194° F.** This method consists in heating a plug of the bituminous substance 5 mm. long, in an open glass tube, 6-7 mm. internal diameter, and about 8 cm. long, the plug supporting 5 g. mercury, and the tube being immersed in a vessel of water, the level of which reaches approximately the center of the mercury column. In making the test, a thermometer is suspended in the liquid, so its bulb will be at the same level as the plug of bituminous material. The thermometer is supported in a separate glass tube of the same thickness and diameter as the other tube, but differing therefrom in having its lower end sealed, and containing sufficient mercury to surround the bulb. The water is heated at a uniform rate of 4° F. per minute, and the temperature at which the mercury drops through the plug of bituminous material recorded as its fusing temperature. The tube containing the bituminous substance may have a mark etched 5 mm. from the end, as a convenient guide for the quantity of bituminous material to be introduced. The plug of bituminous material may be introduced into the tube by inverting it and inserting from its lower end a well-fitting cork or wooden plug fastened to a stiff wire. The mercury is poured on same, and the plug raised or lowered until the meniscus of the mercury coincides with the mark etched on the tube. The bituminous material is then melted at a temperature slightly above its fusing-point and poured on top of the mercury, to completely fill the tube, which should be warmed slightly. When cool, the bituminous material is levelled off even with the end of the tube, whereupon the tube is inverted and the plug withdrawn. This is illustrated in Fig. 146.

The mercury is measured from a heavy-walled capillary tube of 1 mm. bore, terminating in a three-way cock, and calibrated to hold exactly 5 g. mercury at room temperature. The short limb of the tube is connected with a movable reservoir containing mercury, the height of which is adjusted so the mercury in the capillary tube exactly reaches the graduation.

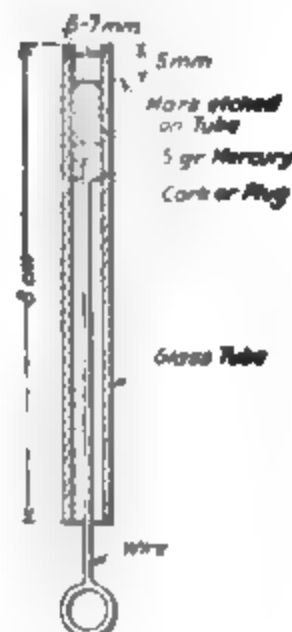


FIG. 146.—Method of Filling K. & S. Fusing-Point Tubes.

<sup>1</sup> The terms "fusing-point" and "softening point" have been used throughout the text in place of the phrase "melting-point," since the former are more expressive of the behavior of fusible bituminous substances under the influence of heat. They pass gradually from the solid to the liquid condition, the transition taking place slowly, owing to the heterogeneous character of the substances present. The phrase "melting-point" is more appropriately applied to chemical substances having a definite composition, which melt sharply, and within a narrow temperature range.

<sup>2</sup> Chem. Ind., 26, 55, 1903.

<sup>3</sup> B. M. Margosches, Chem. Rev. Fett-Harz-Ind., 11, 277, 1904; M. Wendriner, Z. angew. Chem., 18, 622, 1905; E. Graefe, Chem. Zeit., 30, 298, 1906; Bauert, Chem. Zeit., 29, 382, 1905; Offermann, Petroleum, 6, 2117, 1910; L. Barta, Petroleum, 7, 158, 1911; V. Abeles, Chem. Zeit., 38, 249, 1914.

<sup>4</sup> "Improved Instruments for the Physical Testing of Bituminous Materials," by Herbert Abraham, Proc. Am. Soc. Testing Materials, 9, 575, 1909; 11, 673, 1911.

## 1306 EXAMINATION OF BITUMINOUS SUBSTANCES

The heating is conveniently effected by means of a resistance cell consisting of beaker 75 mm. diameter by 100 mm. high, carrying 400 cc. water to which are add 4 drops of concentrated sulphuric acid. The apparatus is assembled as shown in F 147. A direct current of 110 volts is used in conjunction with a rheostat provided wi

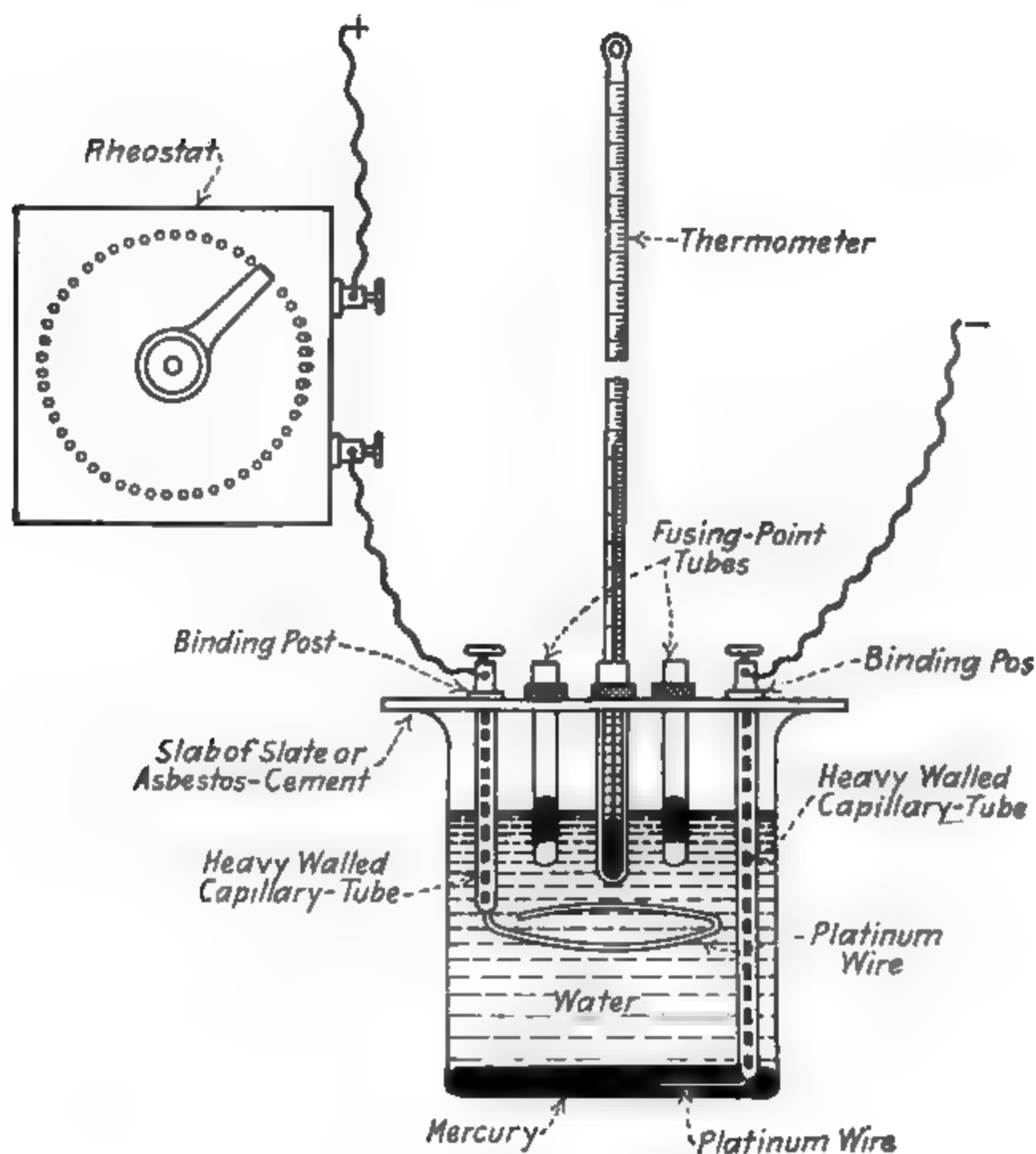


FIG. 147. Resistance Cell for Fusing-point Determination.

25 to 35 notches, having a carrying capacity ranging from  $\frac{1}{2}$  up to 100 amperes (corresponding to a resistance of 220 down to 1.1 ohms).<sup>1</sup>

<sup>1</sup> Private communication from Mr. Dozier Finley, Emeryville, Cal.

A convenient device for controlling the temperature consists of a clock from which the hour hand has been removed, and the dial graduated in 240 divisions representing degrees Fahrenheit. The rise in temperature is synchronized with the minute hand of the clock and controlled by the rheostat to increase *exactly*  $4^{\circ}$  F. per minute. The initial temperature of the water should be at least  $25^{\circ}$  F. lower than the fusing-point of the material to be examined. Six tests may be run simultaneously.

*Substances Fusing above  $194^{\circ}$  F.* In this case the heating is performed by a direct flame, as illustrated in Fig. 148, the water being replaced with castor oil which may be

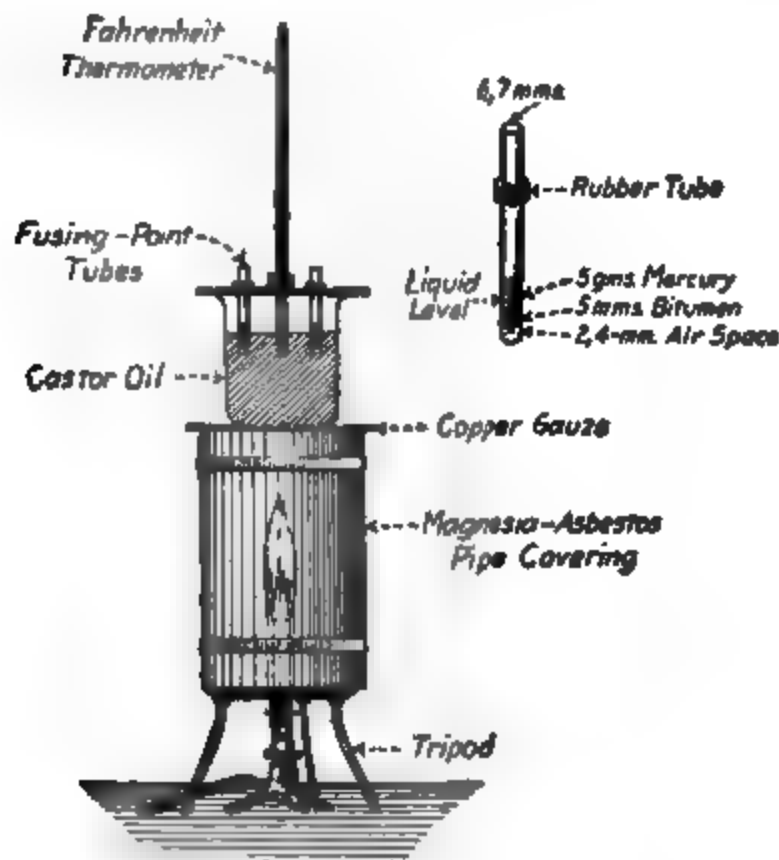


FIG. 148.—K. and S. Tester for High Fusing-Point Substances.

heated safely to about  $600^{\circ}$  F. This method may be used for determining the fusing-point of asphaltites including grahamite. A small quantity of the high fusing-point bituminous material is powdered and compressed in the lower end of the fusing-point tube, whereupon it is carefully heated above the flame of a burner, until the plug of bituminous material softens and fuses to the tube, which is evidenced by the color changing from a dull to a glossy black. The tube is then stood upright against a block of wood, a snug-fitting glass rod inserted in the upper end, and pressed against the softened bituminous material to compact it into a solid mass 7 to 9 mm. long. On cooling, the plug is then carefully scraped from the lower end of the tube until *exactly* 5 mm. remains, leaving an air space 2 to 4 mm. between the plug and the lower end of the tube. Care should be taken when suspending the fusing-point tube in the heating bath to allow the free space below the plug to remain filled with air, otherwise oil will come in contact with, and prematurely soften the bituminous material. The bath is heated at the uniform speed of  $4^{\circ}$  F. per minute.<sup>1</sup>

<sup>1</sup> "Improved Instruments for the Physical Testing of Bituminous Materials," Proc. Am. Soc. Testing Materials, 11, 674, 1911.

## 1308 EXAMINATION OF BITUMINOUS SUBSTANCES

**Ball and Ring Method.<sup>1</sup>** This method has been adopted by the American Society for Testing Materials. The apparatus is illustrated in Fig. 149 and consists of the following: "(a) A brass ring 15.875 mm. ( $\frac{5}{8}$  in.) in inside diameter and 6.35 mm. ( $\frac{1}{4}$  in.) deep; thickness of wall, 2.38 mm. ( $\frac{3}{32}$  in.); permissible variation on inside diameter and thickness of ring, 0.25 mm. (0.01 in.). This ring shall be attached in a convenient manner to a No. 15 B. & S. gage brass wire (diameter 1.79 mm. = 0.0703 in.). (b) A steel ball 9.53 mm. ( $\frac{3}{8}$  in.) in diameter weighing between 3.45 and 3.55 g. (c) A glass vessel, capable of being heated, not less than 11 cm. (4.13 in.) in diameter by 14 cm. (5.51 in.) deep.<sup>2</sup> (d) A thermometer which shall conform to the following specifications: Total length 370–400 mm., diameter 6.5–7.5 mm., bulb length not over 14 mm., bulb diameter 4.5–5.5 mm. The scale shall be engraved upon the stem of the thermometer, shall be clear cut and distinct, and shall run from 32° to 176° F. in 1/10° F. divisions. It shall commence not less than 7.5 cm. above the bottom of the bulb. The thermometer shall be furnished with an expansion chamber at the top and have a ring for attaching tags. It shall be made of a suitable quality of glass and be so annealed as not to change its readings under conditions of use. It shall be correct to 0.5° F. as determined by comparison at full immersion with a similar thermometer calibrated at full immersion by the U. S. Bureau of Standards."

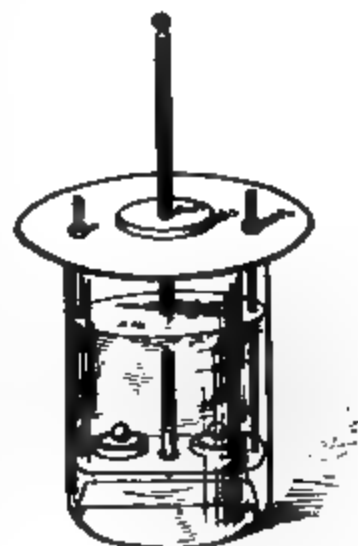


FIG. 149.

"The sample shall be melted and stirred thoroughly, avoiding incorporating air bubbles in the mass, and then poured into the ring so as to leave an excess on cooling.

The ring, while being filled, should rest on a brass plate which has been amalgamated to prevent the bituminous material from adhering to it. After cooling, the excess material shall be cut off cleanly with a slightly heated knife."

*Substances Fusing below 194° F.* "Assemble the apparatus as shown in Fig. 149. Fill the glass vessel to a depth of substantially 8.25 cm. (3.25 in.) with freshly boiled, distilled water at 41° F.<sup>3</sup> Place the ball in the center of the upper surface of the material

<sup>1</sup> "Standard Method for Determination of Softening Point of Bituminous Materials other than Tar Products" (Serial Designation: D 36-19), Am. Soc. Testing Materials, Standards for 1919.

<sup>2</sup> A 600-cc. beaker, Griffin low form, meets this requirement.

<sup>3</sup> The use of freshly boiled distilled water is essential, as otherwise air bubbles may form on the specimen and affect the accuracy of the results.

in the ring and suspend it in the water so that the lower surface of the filled ring is exactly 2.54 cm. (1 in.) above the bottom of the glass vessel<sup>1</sup> and its upper surface is 5.08 cm. (2 in.) below the surface of the water. Allow it to remain in the water for 15 minutes before applying heat. Suspend the thermometer so that the bottom of the bulb is level with the bottom of the ring and within 0.635 cm. ( $\frac{1}{4}$  in.) but not touching the ring. Apply the heat in such a manner that the temperature of the water is raised 9° F. each minute.<sup>2</sup>

"The temperature recorded by the thermometer at the instant the bituminous material touches the bottom of the glass vessel shall be reported as the softening point."

*Substances Fusing above 194° F.* "Use the same method as given above, except that glycerin shall be used instead of water."

The limit of accuracy of the test is  $\pm 1.0^\circ$  F. The resistance cell described may be used to good advantage in the Ball and Ring method.

Tests made by the author indicate that the Ball and Ring fusing-points range 15 to 25° F. higher than those obtained by the K. and S. method. This relationship holds true regardless of whether the fusing-point of the material is low or high.

**Cube Method.** This method is restricted to testing tar-pitches.<sup>3</sup>

*For Pitches Fusing below 170° F.* The following method has been proposed by the American Society for Testing Materials:<sup>4</sup>

"The apparatus is illustrated in Fig. 150 and shall consist of the following: (a) A mold suitable for forming a 12.7 mm. ( $\frac{1}{2}$  in.) cube of pitch; (b) an L-shaped right-angled hook made of No. 12 B. & S. gage copper wire (diameter 2.05 mm = 0.0808 in.) the foot of which shall be 2.54 cm. (1 in.) long; (c) a glass vessel, capable of being heated, not less than 8.5 cm. (3.34 in.) in diameter and measuring 10.5 cm. (4.13 in.) in depth from the bottom of the flare;<sup>5</sup> (d) a thermometer which shall conform to the following specifications: total length 370–400 mm., diameter 6.5–7.5 mm., bulb length not over 14 mm., bulb diameter 4.5–5.5 mm. The scale shall be engraved upon the stem of the thermometer, shall be clear cut and distinct, and shall run from 32 to 176° F. in  $1/10^\circ$  F. divisions. It shall commence not less than 7.5 cm. above the bottom of the bulb. The thermometer shall be furnished with an expansion chamber at the top and have a ring for attaching tags. It shall be made of a suitable quality of glass and be so annealed as not to change its readings under conditions of use. It shall be correct to 0.45° F. as determined by comparison at full immersion with a similar thermometer calibrated at full immersion by the U. S. Bureau of Standards."

<sup>1</sup> A sheet of paper placed on the bottom of the glass vessel and conveniently weighted will prevent the bituminous material from sticking to the glass vessel, thereby saving considerable time and trouble in cleaning.

<sup>2</sup> Rigid adherence to the prescribed rate of heating is absolutely essential to secure accuracy of results. The rate of rise of temperature shall be uniform and shall not be averaged over the period of the test. The maximum permissible variation for any minute period after the first three shall be  $\pm 0.9^\circ$  F. All tests in which the rate of rise in temperature exceeds these limits shall be rejected.

<sup>3</sup> "Methods for Testing Coal Tar, and Refined Tars, Oils, and Pitches Derived Therefrom," by S. R. Church, J. Ind. Eng. Chem., 3, 230, 1911; 5, 195, 1913.

<sup>4</sup> "Tentative Method for Determination of Softening Point of Tar Products—Cube in Water Method" (Serial Designation: —19 T.), Proc. A. S. T. M., 19, Part 1, 764, 1919.

<sup>5</sup> A 600-cc. beaker, Griffin low form, meets this requirement.

## 1310 EXAMINATION OF BITUMINOUS SUBSTANCES

"The pitch shall be formed into a 12.7 mm. ( $\frac{1}{2}$  in.) cube, truly shaped and with sharp edges, either by melting and pouring, or softening and pressing into the mold. In all cases an excess of pitch shall be used and the surplus material shall be cut off cleanly with a slightly heated knife. The harder pitches specified can ordinarily be molded at room temperature, the softer pitches in water at about 40° F. If they are melted, they should first be thoroughly stirred, avoiding incorporating air bubbles in

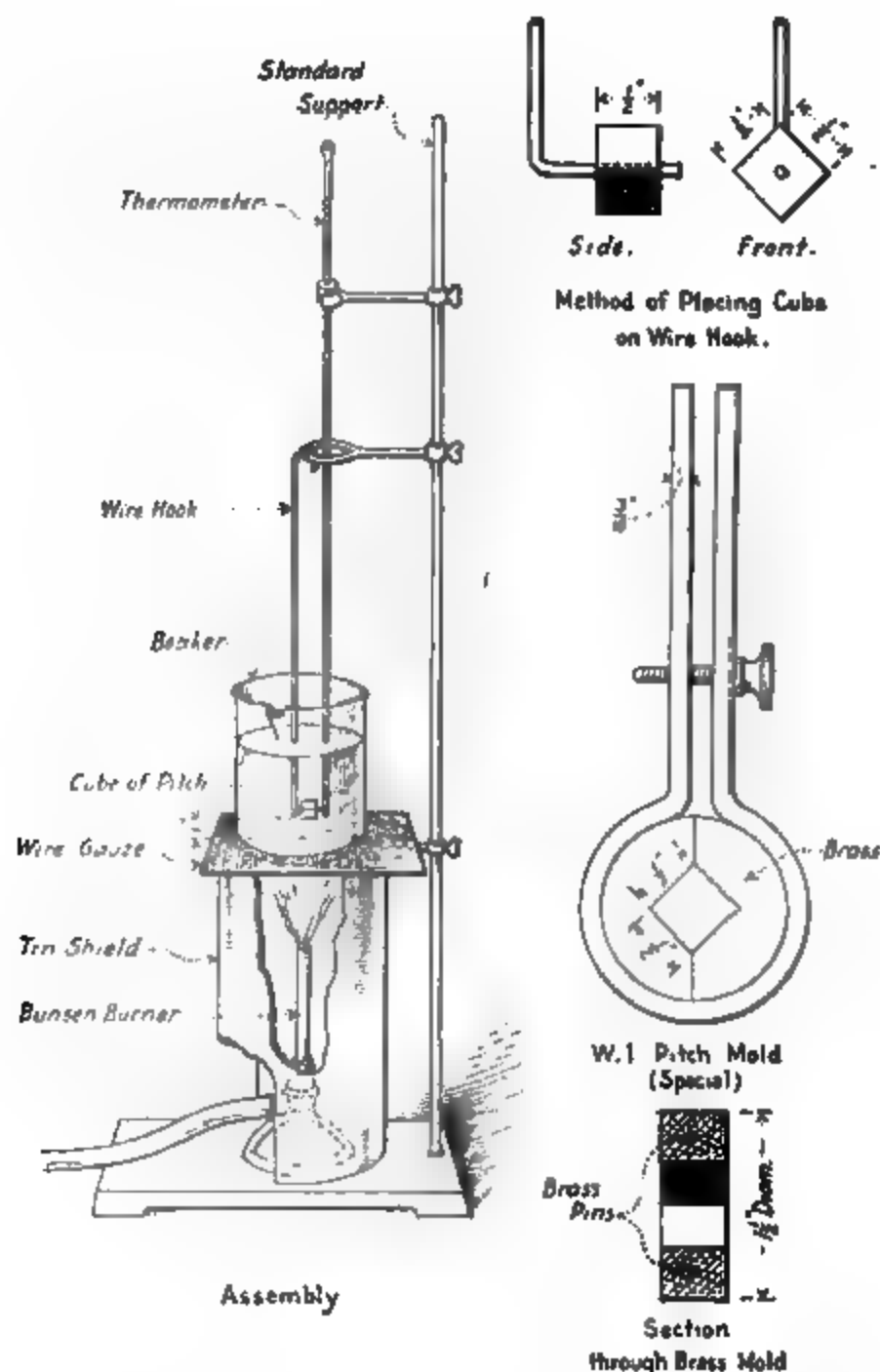


FIG. 150.—Cube-in-water Method for Low Fusing-point Substances.

the mass, and then poured into the mold so as to leave an excess on cooling. The mold should rest on a brass plate and the surface of the plate and the interior surfaces of the mold should be amalgamated to prevent the pitch from adhering to them."

"Assemble the apparatus as shown in Fig. 150. Fill the glass vessel with freshly boiled distilled water<sup>1</sup> to a depth of substantially 9.5 cm. (3.75 in.). With pitches having softening points below 109.4° F. the temperature of the water shall be 40° F., and with pitches having softening points between 109.4° and 170° F. the temperature of the water shall be 60° F. Place the cube of pitch on the wire as shown and suspend it in the water so that its lower edge is exactly 2.54 cm. (1 in.) above the bottom of the glass vessel<sup>2</sup> and its upper edge is 5.08 cm. (2 in.) below the surface of the water. Allow it to remain in the water for 15 minutes before applying heat. Suspend the thermometer so that the bottom of the bulb is level with the bottom edge of the cube of pitch and within 0.635 cm. ( $\frac{1}{4}$  in.), but not touching the cube. Apply the heat in such a manner that the temperature of the water is raised 9° F. each minute.<sup>3</sup> The temperature recorded by the thermometer at the instant the pitch touches the bottom of the glass vessel shall be reported as the softening point."

"The limit of accuracy of the test is  $\pm 0.9^\circ$  F."

*For Pitches Fusing above 170° F.* The heating is performed in an air bath in the apparatus illustrated in Fig. 151. The cube should be suspended in line with the

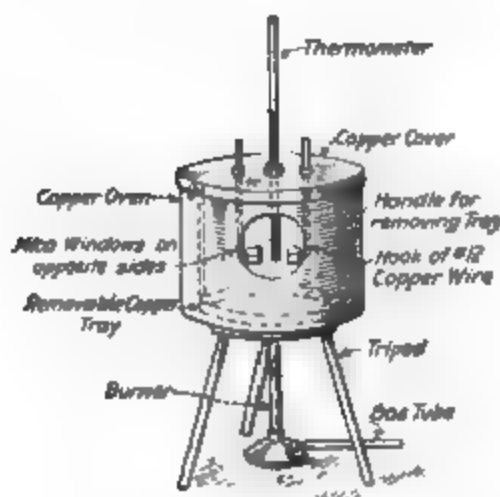


FIG. 151.—Cube-in-Air Method for High Fusing-point Substances.

observation windows, and the thermometer bulb brought to the same level. The temperature is raised 9° F. per minute, and recorded by the thermometer when the cube drops 1 in. To make the results obtained by this method correspond approximately with those obtained in water, 12° F. should be added to the observed fusing-point.

Investigations of the relationship between the Cube and the Ball and Ring methods indicate that the results vary considerably, depending largely upon the nature of the products tested and their fusing-points. No exact factors can be given.

<sup>1</sup> The use of freshly distilled water is essential, as otherwise air bubbles may form on the cube and retard its sinking.

<sup>2</sup> A sheet of paper placed on the bottom of the glass vessel and conveniently weighted will prevent the pitch from sticking to the glass vessel, thereby saving considerable time and trouble in cleaning.

<sup>3</sup> Rigid adherence to the prescribed rate of heating is absolutely essential in order to secure accuracy of results. The rate of rise of temperature shall be uniform and shall not be averaged over the period of the test. The maximum permissible variation for any minute period after the first three shall be  $\pm 0.9^\circ$  F. All tests in which the rate of rise in temperature exceeds these limits shall be rejected.



## Volatile Matter.

The following method of procedure has been adopted by the American Society for Testing Materials,<sup>1</sup> for determining the loss in weight (exclusive of water) of oil and asphaltic compounds when heated as described. The material under examination must therefore first be tested for water, and if water is found to be present, it must be removed by suitable methods of dehydration before the material is subjected to the loss on heating test; or another sample obtained which is free from water.

"The oven may be either circular or rectangular in form and may be heated by either gas or electricity. Its interior dimensions shall be as follows: height, not less than 40.64 cm. (16 in.), width and depth or diameter, at least 40.8 cm. (2 in.) greater than the diameter of the revolving shelf. It shall be well ventilated and shall be fitted with a window in the upper half of the door, so placed and of sufficient size to permit the accurate reading of the thermometer without opening the door. It shall also be provided with a perforated circular shelf preferably of approximately 24.8 cm. (9.75 in.) in diameter. (A recommended form of aluminium shelf is shown in Fig. 152.) This shelf shall be placed in the center of the oven and shall be suspended by a vertical shaft and provided with mechanical means for rotating it at the rate of 5 to 6 revolutions per minute. It shall be provided with recesses equidistant from the central shaft in which the tins containing the samples are to be placed."

"The thermometer shall be between 12.7 cm. (5 in.) and 15.24 cm. (6 in.) in length and the mercury bulb shall be from 10 mm. (0.39 in.) to 15 mm. (0.59 in.) in length. The scale shall be engraved on the stem, shall be clear cut and distinct, and shall run from 302° to 347° F. in 1° F. divisions and shall commence substantially 3.81 cm. (1 1/2 in.) above the top of the bulb. Every fifth degree shall be larger than the intermediate ones and shall be numbered . . . . It shall be made of a suitable quality of glass and be so annealed as to not change its readings under conditions of use. It shall be correct to 0.45° F. as determined by comparison at full immersion with a similar thermometer calibrated at full immersion by the U. S. Bureau of Standards."

"The container in which the sample is to be tested shall be of tin, cylindrical in shape, and shall have a flat bottom. Its inside dimensions shall be substantially as follows: diameter 55 mm. (2.17 in.), depth, 35 mm. (1.38 in.)."

"The sample as received shall be thoroughly stirred and agitated, warming if necessary, to insure a complete mixture before the portion for analysis is removed. Weigh 50 g. of the water-free material to be tested into a tared container of the form described. Bring the oven to a temperature of 325° F., and place the tin box containing the sample in one of the recesses of the revolving shelf. The thermometer shall be immersed for the depth of its bulb in a separate 50 g. sample of the material under test, placed in a similar container, and shall be conveniently suspended from the vertical shaft. This sample shall rest in one of the recesses upon the same shelf and revolve with the sample or samples under test. Then close the oven and rotate the shelf 5 to 6 revolutions per minute during the entire test. Maintain the temperature at 325° F. for 5 hours, then remove the sample from the oven, cool and weigh, and calculate the loss due to volatilization. During the 5-hour period the temperature shall not vary more than 2° F. All tests showing a greater variation in temperature shall be rejected."

<sup>1</sup> "Tentative Test for Loss on Heating of Oil and Asphaltic Compounds" (Serial Designation: D 6-19 T.), A. S. T. M. Tentative Standards for 1919.

<sup>2</sup> A 3-oz. Gill style ointment box, deep pattern, fulfills these requirements.

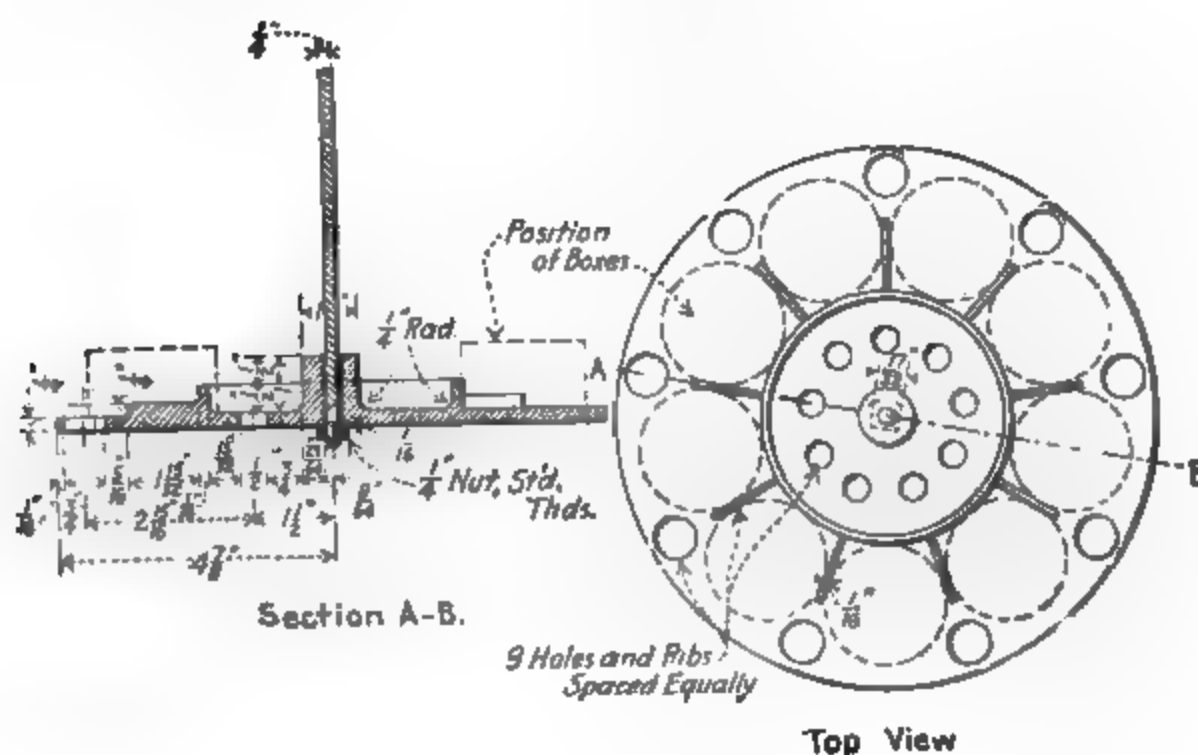
<sup>3</sup> If additional periods of heating are desired, it is recommended that they be made in successive increments of 5 hours each.

"Up to 5 per cent loss in weight the results obtained may be considered as correct within 0.5. Above 5 per cent loss in weight the numerical limit of error increases 0.01 or every 0.5 per cent increase in loss by volatilization as follows:

Volatilization Loss, per cent	Numerical Correction	True Volatilization Loss, per cent
5.0.....	$\pm 0.50$	4.50 to 5.50
5.5.....	$\pm 0.51$	4.91 to 6.01
6.0.....	$\pm 0.52$	5.48 to 6.52
10.0.....	$\pm 0.60$	9.40 to 10.60
15.0.....	$\pm 0.70$	14.30 to 15.70
25.0.....	$\pm 0.90$	24.10 to 25.90
40.0.....	$\pm 1.20$	38.80 to 41.20

"Under ordinary circumstances a number of samples having about the same degree of volatility may be tested at the same time. Samples varying greatly in volatility should be tested separately. Where extreme accuracy is required not more than one material should be tested at one time and duplicate samples of it should be placed simultaneously in the oven. Such duplicates shall check within the limits of accuracy given above. Results obtained on samples showing evidences of foaming during the test shall be rejected."

"When the penetration of the sample after heating is required, melt the residue at the lowest possible temperature and thoroughly mix by stirring, taking care to avoid incorporating air bubbles in the mass. Then bring it to the standard temperature and test as prescribed."



From A. S. T. M. Standards.

FIG. 152.—Shelf for Volatility Oven.

The oven ordinarily employed for determining the volatile matter, illustrated in Fig. 153, is composed of a cylindrical vessel with a hinged cover, surrounded by an insulated jacket, with an air-space in between acting as a flue to carry off the hot gases generated by the ring-burner underneath. The temperature may be conveniently regulated by a mercury thermostat.

**Flash-point.**

The flash-point procedure is used primarily for determining the adaptability of bituminous substances for certain definite usages, and serves as a criterion of the fire hazard.

A number of flash-point testers have been proposed, of which the following are most generally used:

**Pensky-Martens Closed Tester.** This apparatus has been adopted as standard by the Government of the United States, and foreign governments for testing high flash-point bituminous materials. The instrument is illustrated in Fig. 154, and consists



Courtesy of Wm. Boekel & Co.  
FIG. 153.—Volatility Oven.

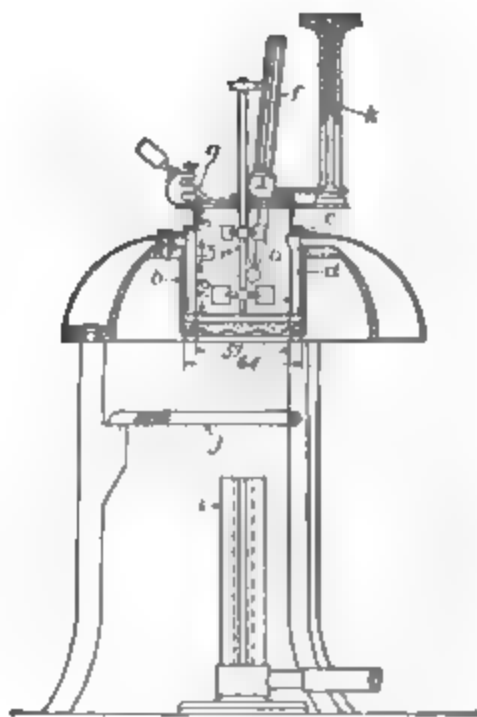


FIG. 154.—Pensky-Martens Closed  
Flash-point Tester.

of an oil cup *a*, in a metal heating vessel *b*, surrounded with a flanged top to prevent loss of heat by radiation. An orifice *c* permits the overflow of the oil into the jacket *d* between the oil cup and the heating vessel. It is likewise provided with a mechanical stirring device *e*, the thermometer *f*, the test flame *g*, burner *i*, wire screen *j*, and spring *k* to work the slide under the test flame.

The approximate flash-point is ascertained by a preliminary test. The melted bituminous substance is poured into the Pensky-Martens tester, which should be perfectly level, taking care not to splash any on the sides of the cup, or to cause any froth on the surface. All bubbles should be pricked with a heated wire. The test flame is then regulated to correspond in size with the ivory bead on the cover (to burn 0.1 cu.ft. coal gas per hour). The burner *i* is lit, and the contents heated rapidly at first until the temperature reaches 50° F. below the expected flash-point, whereupon the rise in temperature should be controlled to increase exactly 5° F. per minute. At each degree the milled head *k* is turned and the flame *g* tilted into the cup for exactly one second. The test is continued until the flash-point occurs. Any slight flickering or spreading of the flame is ignored. The end point is evidenced by an unquestionable flash. The apparatus should be protected from draughts, and the sample stirred continuously during the test. If the thermometer is graduated to read for total immersion, the stem-correction should be applied. When this is done, it is suggested that "corr." be added to the reading, thus: "Flash 379° F. corr."

A simplified form of Pensky-Martens tester for approximately determining the flash-point, consists of a glass beaker or metal cup having the same dimensions, namely 5.0 cm. in diameter, and 5.5 cm. in depth, filled to within 1.8 cm. of its upper rim with the material to be tested. This is supported on a sand bath and the thermometer bulb immersed in the bituminous material without, however, touching the sides or bottom. The test flame is adjusted to a 3 mm. cross-section, and the test performed exactly as described for the Pensky-Martens tester.<sup>1</sup>

**Cleveland Open Tester.** This apparatus is described on p. 1120.

**New York State or Elliot Closed Tester.** The method of using this tester is described on p. 1109. For testing bituminous substances, the rise in temperature is carefully regulated to 10° F. per minute.

### Fixed Carbon

The same procedure is followed as for testing coal, described on p. 1218 ("Volatile Combustible Matter"), also p. 1222.

### Distillation Test

**Flask Method of Distillation.** If water is present, the bituminous material must first be dehydrated. This may be conveniently performed by distilling 500 cc. in an 800-cc. copper still, provided with a water-cooled condenser, the distillate being caught in a 200-cc. separatory funnel. When all the water is expelled, the distillate is allowed to settle, the water drawn off and the oils returned to the residue in the still after the contents have cooled below 212° F.

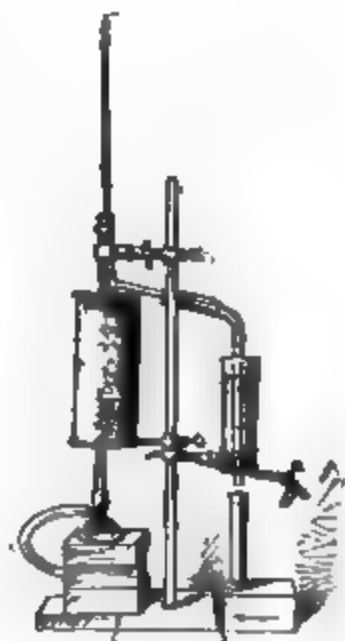
The apparatus as assembled is illustrated in Fig. 155. It consists of a standard 250-cc. Engler distilling flask.

The condenser tube shall have the following dimensions: adapter 70 mm.; length of straight tube 185 mm.; width of tube 12-15 mm.; width of adapter end of tube 20-25 mm.

A carefully standardized thermometer should be used. The cylinder used for collecting the distillate shall have a capacity of 25 cc. and be graduated in 0.1 cc. The burner should be provided with a tin shield, having a small hole for observing the flame. The thermometer bulb should be placed opposite the middle of the tubulature. Pour 100 cc. of the dehydrated bituminous material into the Engler flask and weigh. Then commence to distil at the rate of 1 cc. per minute, changing the receiver as the mercury column passes the following fractioning points, reporting the fractions by weight and by volume:

Start to 110° C.; 110-170° C.; 170-235° C.; 235-270° C.; 270-300° C.; and residue.

The residue is weighed after the distillation is completed and the flask cooled.<sup>2</sup>



From A. S. T. M. Standards.

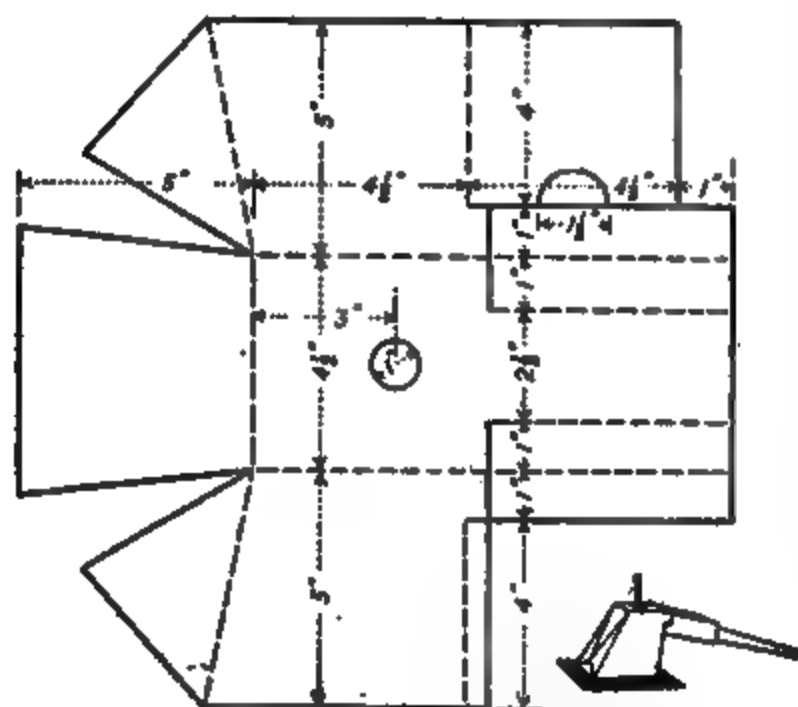
FIG. 155. — Flask Method of Distillation.

<sup>1</sup> "Flash Point of Oils," by I. C. Allen and A. S. Crossfield, Tech. Paper No. 49, Petroleum Technology 10, Dept. of Interior, Bureau of Mines, Wash., D. C., 1913.

<sup>2</sup> "Standard Method for Distillation of Bituminous Materials Suitable for Road Treatment" (Serial Designation: D 20-18), 1918 Book of A. S. T. M. Standards, 669.

## 1316 EXAMINATION OF BITUMINOUS SUBSTANCES

**Retort Method of Distillation.** This method is adapted principally for analyzing creosote oils suitable for impregnating timber.<sup>1</sup> The distillation is performed in a glass retort, having a capacity of 250–290 cc. (measured by placing the retort with the bottom of the bulb and the end of the offtake in the same horizontal plane and pouring water into the bulb through the tubulature until it overflows through the offtake). The length of the offtake should be 25–30 cm., its internal diameter next to the bulb approximately 2.85 cm., and the diameter at the open end approximately 1.25 cm. The diameter of the tubulature should be approximately 1.9 cm.



From A. S. T. M. Standards.

FIG. 156.—Asbestos Shield for Retort.

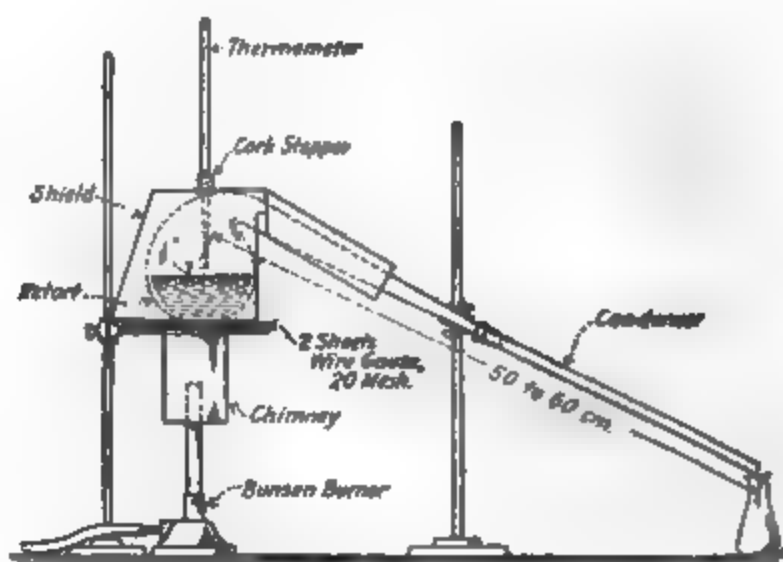
dimensions illustrated in Fig. 156. The receiver shall consist of Erlenmeyer flasks of 50–100 cc. capacity, and the thermometer shall be carefully standardized.

The apparatus is assembled as illustrated in Fig. 157. Exactly 100 g of dehydrated creosote oil are distilled at the rate of not less than 1, nor more than 2 drops per second, the distillate being collected and weighed in the receiver. The condenser tube should be warmed whenever necessary to prevent the accumulation of solid distillate, and the receiver changed as the mercury passes the dividing temperatures of the following fractions: 210, 235, 270, 315 and 355° C. When the temperature registers 355° C., the flame shall be removed from the retort, and any oil which has condensed in the offtake drained into the 355° fraction. The retort is cooled and reweighed to ascertain the amount of residue, which is generally tested by the float test. The various fractions should be reported by weight and also by volume, and their specific gravities calculated.

<sup>1</sup> "Standard Method for Sampling and Analysis of Creosote Oil" (Serial Designation: D 38-18), A. S. T. M. Standards Adopted in 1918, 727.

The condenser tube shall have the following dimensions: diameter of small end 12.5 mm. with a variation of 1.5 mm.; diameter of large end 28.5 mm. with a variation of 3.0 mm.; length 360 mm. with a variation of 4.0 mm.

The asbestos shield for the retort shall have the form and dimensions illustrated in Fig. 156. The receiver shall consist of Erlenmeyer flasks of 50–100 cc. capacity, and the thermometer shall be carefully standardized.



From A. S. T. M. Standards.

FIG. 157.—Retort Method of Distillation.

## SOLUBILITY TESTS

## Solubility in Carbon Disulphide

With native asphalt containing over 10 per cent of mineral matter, it is advisable to separate the portion soluble in carbon disulphide for ascertaining its physical characteristics, fusing-point, and sometimes fixed carbon.

The tests generally employed for this purpose have been devised by the Am. Soc. Testing Materials<sup>1</sup> and are substantially as follows, deviating slightly in phraseology.

The bituminous material should first be freed from moisture. If semi-solid to solid it may be heated in an oven 125° C. for 1 hour, provided it is substantially free from volatile matter at this temperature. If volatile materials are present, it should be dehydrated by distillation at a low temperature, the water-free distillate being returned to the residue, and thoroughly incorporated with it.

Sufficient of the dehydrated material to insure the presence of 1-2 g. soluble in carbon disulphide is weighed into a 150-cc. tared Erlenmeyer flask, and 100 cc. of c.p. carbon disulphide poured into the flask in small portions, with continuous agitation until all the lumps disappear and nothing adheres to the bottom. The flask is then loosely corked and set aside. From this point on, one of two methods may be followed, depending on whether or not the bituminous material contains a substantial quantity of finely divided insoluble matter.

*Procedure Used in the Presence of Substantial Quantities of Finely Divided Insoluble Matter.* The flask is set aside to settle for 48 hours, and the solution decanted into a second tared flask, pouring off as much of the solvent as possible without disturbing the residue. The contents of the first flask are again treated with a quantity of carbon disulphide, shaken as before, and both the first and second flasks allowed to settle for another 48 hours. The liquids in both flasks are then carefully decanted upon a weighed Gooch crucible (measuring 4.0 cm. wide at the top, tapering to 3.2 cm. at the bottom, and 2.5 cm. deep), carrying freshly ignited long-fibered amphibole (asbestos) compacted in a layer not over  $\frac{1}{4}$  in. No vacuum is to be used in filtering, and the temperature of the liquid kept between 65 and 77° F. The residue remaining on the filter is thoroughly washed with carbon disulphide until the filtrate becomes clear. The flasks are again shaken with fresh carbon disulphide, allowed to settle for 24 hours, or until it is seen that a good submersion has taken place, and thereupon decanted through the filter. The residues remaining in both flasks are washed until the washings are practically colorless, all washings being passed through the Gooch crucible.

*Procedure Followed with Materials Containing Little to no Finely Divided Insoluble Matter.* This method is used for rapid work where the bituminous material does not contain insoluble matter which would clog the pores of the filter. After adding the carbon disulphide, the flask is set aside for 15 minutes, whereupon it is filtered through a weighed Gooch crucible. The liquid must be decanted with care, and the decantation stopped at the first sign of sediment coming over. The sides of the flask are washed with a small amount of fresh carbon disulphide, and the sediment caught on the filter, using a "policeman," if necessary, to remove all adhering material. Then wash residue on filter with carbon disulphide until the washings are colorless, and continue the suction until the odor of carbon disulphide is scarcely detectable. The outside of the crucible is cleaned by a cloth moistened with a small amount of the solvent.

In both procedures, the crucible and contents, likewise the two flasks in the first method, are heated for one-half hour at 220° F., cooled in a desiccator and weighed. The difference between the weight of the dehydrated material taken for analysis and the weight of the residue, represents the proportion soluble in carbon disulphide.<sup>2</sup>

<sup>1</sup> "Standard Test for Soluble Bitumen" (Serial Designation: D 4-11), A. S. T. M. Standards Adopted in 1916, 528; A. S. T. M. Standards 1918, 630; "Tentative Specifications for Asphalt for Use in Damp-proofing and Water-proofing" (Serial Designation: D 40-17 T), Proc. Am. Soc. Testing Materials, 17, Part I, 714, 1917.

<sup>2</sup> For a discussion of the method, see "A Study of Certain Methods for Determining Total Soluble Bitumen in Paving Materials," by S. Avery and R. Corr, J. Am. Chem. Soc., 28, 648, 1906, "The Proximate Composition and Physical Structure of Trinidad Asphalt, with Special Reference to the Behavior of Mixtures of Bitumen and Fine Mineral Matter," by Clifford Richardson, Proc. Am. Soc. Testing Materials, 6, 500, 1906, "The Determination of Soluble Bitumen," by Hubbard and Reeve, Proc. Am. Soc. Testing Materials, 10, 420, 1910, "The Bitumen Content of Coarse Bituminous Aggregates," by Prevost Hubbard, Proc. Int. Assoc. Testing Materials, XXV-2, 1912.

## 1318 EXAMINATION OF BITUMINOUS SUBSTANCES

The author finds that in the presence of large quantities of finely divided insoluble matter, the method may be materially shortened by adding a weighted quantity (about twice the weight of bituminous material) of freshly ignited, long-fibered amphibole to the bituminous substance in the first flask. On shaking with carbon disulphide, the asbestos serves to dilute the insoluble matter, preventing the latter from clogging the pores of the filter, and accordingly reducing the time of filtration. In many cases this procedure may be adopted to good advantage.

The total weight of the insoluble matter obtained in the foregoing test, includes both the non-mineral matter insoluble in carbon disulphide, and the mineral matter. The former is determined by igniting the residue in the Gooch crucible (to which must be added the residues remaining in the flasks) until no carbonaceous particles remain, leaving only the mineral ash. Add a few drops of ammonium carbonate solution to the residue, ignite for a few minutes at a red heat, cool in a desiccator, and weigh. The loss in weight on ignition represents the "non-mineral matter insoluble in carbon disulphide."

The residue obtained in the foregoing test represents the mineral constituents. When calcium carbonate is present it is necessary to ignite the residue with ammonium carbonate before finally weighing, as it is claimed that any sulphur present in the bituminous material reacts with the calcium carbonate forming calcium sulphate and calcium sulphide.<sup>1</sup> The loss of any water of hydration from clays, etc., and the oxidation of iron pyrites to ferric oxide, will also affect the results. The mineral matter may be checked by igniting a fresh sample in a platinum crucible to clean ash, adding a few drops of ammonium carbonate, re-igniting and weighing. If the two results do not agree, evaporate the filtrate containing the bituminous matter soluble in carbon disulphide, burn, ignite and weigh the residue. The weight of the ash derived from the bituminous matter soluble in carbon disulphide should be added to the original residue of insoluble mineral matter. This may represent colloidal mineral particles, which are not retained by the filter, or else mineral constituents combined chemically with the bituminous matter.

### Carbenes

The expression "carbenes" has been generally applied to that portion of bituminous substances soluble in carbon disulphide but insoluble in carbon tetrachloride. This term was originally proposed by Clifford Richardson.<sup>2</sup> This test is of value in identifying bituminous substances, gauging their uniformity of supply, for purposes of factory control, and as a criterion of their quality. Certain hard native asphalts and asphaltites, particularly grahamite, normally contain a percentage of carbenes, whereas petroleum asphalts do not show carbenes unless they are overheated, or over-blown. If more than 0.5 per cent is present in petroleum asphalts, their quality is to be regarded as questionable. Carbenes are found in tars and pitches in varying amounts.<sup>3</sup>

This test is carried out by following the same procedure as in determining the solubility in carbon disulphide, but replacing the latter with carbon tetrachloride. The carbon tetrachloride must be free from carbon disulphide, which may be insured by distilling it under a dephlegmator, discarding any distillate below 76° C. The solvent is then filtered through calcium chloride, and any free hydrochloric acid removed by blowing dry air through it.

<sup>1</sup> "Analysis of Calcareous Asphaltum and Paving Mixtures," by Prettnner, *Chem. Zeit.*, **33**, 917 and 926, 1909.

<sup>2</sup> "Carbon Tetrachloride and its Use as a Solution for Differentiating Bitumens," by Clifford Richardson and C. N. Forrest, *J. Soc. Chem. Ind.*, **24**, 310, 1905.

<sup>3</sup> "Some Relations of the Effect of Overheating to Certain Physical and Chemical Properties of Asphalts," by A. W. Hixson and H. E. Hands, *J. Ind. Eng. Chem.*, **9**, 651, 1917; "The Value of the Carbene Requirement in Asphalt Specifications," by L. Kirschbraun, *Munic. Eng.*, **35**, 349, 1909.



The carbon tetrachloride is allowed to act on the bituminous substance overnight, care being taken to keep the vessel in a dark place to protect it from daylight or sunshine.<sup>1</sup> Richardson proposes blowing a gentle current of air through the solution in the dark for 1 hour<sup>2</sup> to coagulate the insoluble matter and assist in the filtration. The difference between the percentages soluble in carbon disulphide and carbon tetrachloride respectively, represents the per cent of "carbenes."

#### Solubility in 88° Petroleum Naphtha

The portion soluble in 88° naphtha has been termed "petrolenes" by some, and "malthenes" by others, whereas the non-mineral constituents insoluble in 88° naphtha are generally referred to as "asphaltenes."

It is important that the petroleum naphtha should be derived from petroleum composed entirely of open-chain hydrocarbons, and test exactly 88° Baumé, equivalent to a specific gravity of 0.638 at 60° F./60° F. At least 85 per cent by volume should distil between 95 and 150° F. The density and character of the naphtha is important, since heavy distillates, or products derived from petroleum containing unsaturated or cyclic hydrocarbons will exert a greater solvent action upon the bituminous substance.

This method is performed in the same manner as for determining the portion soluble in carbon disulphide, 88° petroleum naphtha being substituted for the latter. Hard bituminous substances should be powdered; liquid bituminous substances flowed in a thin layer over the bottom of the flask; and semi-solid to semi-liquid substances heated until fluid and distributed in a thin layer to present a greater surface to the solvent. It is advisable not to use a stirring rod, as this causes the bituminous substance to adhere to the inner surface of the flask and to the rod itself. The operation should take place at room temperature, and away from the direct rays of the sun. The introduction of a weighed portion of long-fibered asbestos to the solution will assist in its filtration.<sup>3</sup>

#### Solubility in Other Solvents.

Solvents other than those mentioned in the foregoing tests, including benzol, mixtures of benzol and toluol, acetone, etc., are occasionally used for identifying bituminous substances or to investigate their adaptability for a given use. The extraction may be carried out hot or cold, but in either event the method used should be clearly stated in reporting the results. If cold, follow the method described under the heading "Solubility in Carbon Bisulphide." If hot, follow the method described for determining "Free Carbon in Tars." Hard and brittle bituminous substances should be powdered. Medium and soft substances should be mixed with five times their weight of long-fibered amphibole (previously ignited) or ten times their weight of 20- to 30-mesh Ottawa silica, to prevent the material fusing together in a solid mass and retard the action of the solvent. Where the hot "extraction is used, the operation is continued for at least six hours, and until no further loss in weight is recorded, whereupon the contents of the filter cup are dried and weighed."

<sup>1</sup> "Studies on the Carbenes," by K. J. Mackenzie, *J. Ind. Eng. Chem.*, 2, 124, 1910; "On the Formation of Carbenes," by D. B. W. Alexander, *J. Ind. Eng. Chem.*, 2, 242 1910.

<sup>2</sup> "The Modern Asphalt Pavement," by Clifford Richardson, 2nd Edition, 546, 1908.

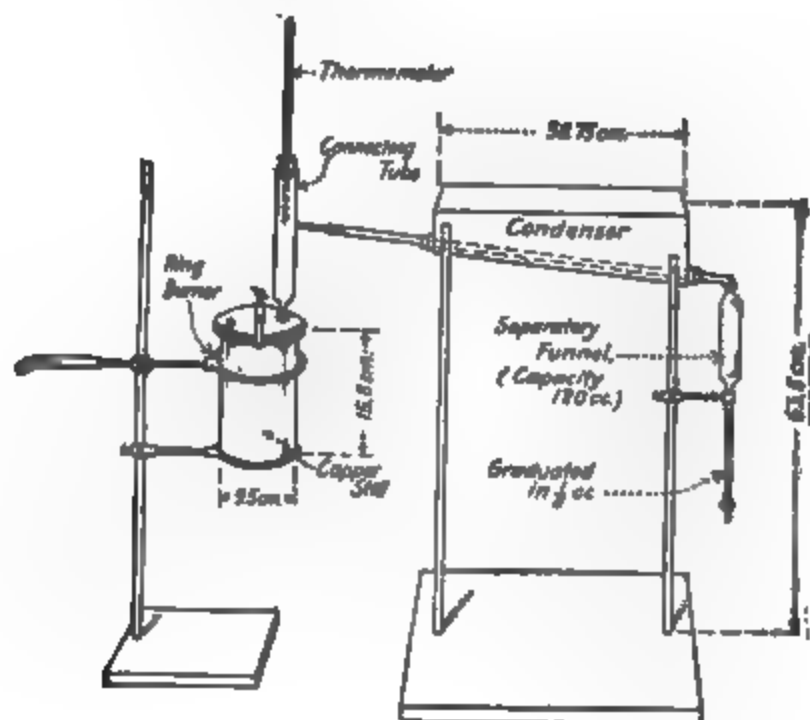
<sup>3</sup> "The Modern Asphalt Pavement," by Clifford Richardson, 2nd Edition, p. 543, 1908; "Laboratory Manual of Bituminous Materials," by Hubbard, 1st Edition, p. 90, 1916.



## CHEMICAL TESTS

## Water

**Substances Distilling at Low Temperatures.** This method is adapted to crude petroleum, tars, creosote oil and other fluid bituminous substances distilling at comparatively low temperatures.<sup>1</sup> The apparatus is set up as shown in Fig. 158. The



From A. S. T. A. Standards.

FIG. 158.—Still for Determining Water.

copper still is provided with a removable flanged top and yoke, which with a paper gasket will form an air-tight joint when clamped into place. The thermometer should be carefully standardized, as provided in the Am. Soc. Testing Materials Standards, 1918, p. 727. The condenser consists of a copper trough carrying a straight-walled glass tube. The separatory funnel has a total capacity of 120 cc. with the outlet graduated in fifths of a cubic centimeter.

Pour 200–500 cc. of the bituminous material into the still and weigh. Clamp the top in place, using a paper gasket moistened with lubricating oil. Apply heat with the ring burner supported just above the level of the bituminous material at the beginning of the test, and then gradually lower it as the water distills over. Continue the distillation until the vapor temperature reaches 205° C. Collect the distillate in the separatory funnel, and let it stand until a clean separation of water takes place. Read off the volume of water, calculate its weight, and figure the per cent present in the crude bituminous material. Draw off the water, and return any light oil to the bituminous matter in the still. The dehydrated material should then be used for further tests.

<sup>1</sup> "Standard Methods for Sampling and Analysis of Creosote Oil" (Serial Designation: D 38-18), A. S. T. M. Standards, Adopted in 1918, 722.

**Substances Distilling at High Temperatures.** This method is adapted to asphalts and other bituminous substances comparatively free from volatile constituents, and incapable of distilling without suffering decomposition.

**Substances Fusing below 300° F.** When it is desired to determine the percentage of moisture without using the residue for other purposes, a convenient method consists in weighing 100 g. into a distilling flask, adding 200 cc. of kerosene in the case of asphaltic products, or toluol in the case of tar products, and warming gently under a reflux condenser until the bituminous substance mixes with the solvent. Cool, add a quantity of dry pumice-stone to prevent bumping, and distil into a graduate until the liquid comes over clear. The distillate is then allowed to settle by gravity, and the volume of water read off directly; or else the water may be withdrawn with a pipette, and weighed. This method is said to be accurate to approximately 0.033 g. of water per 100 cc. of toluol or kerosene present in the distillate.<sup>1</sup>

Where the hydrated material is to be used for further examination, 25 g. are weighed into an Erlenmeyer flask, through which a current of dry illuminating gas is passed, and maintained at 105° C. for 1 hour. The vapors are led through a return condenser maintained at 50° C., and then into a weighed calcium chloride tube. When all the moisture is driven off, the calcium chloride tube is reweighed and the moisture calculated. If constituents are present volatilizing below 50° C., the return condenser should be maintained at a corresponding lower temperature.

**Substances Fusing above 300° F.** In this case the material is comminuted by powdering (to about 60 mesh) or shaving, and a weighed quantity spread in a thin layer on glass and maintained in an oven at 125° C. for 1 hour, or until the weight becomes constant. If the substance is oxidizable in air, it should be heated in an atmosphere of illuminating gas. Cool in a desiccator, reweigh and calculate the per cent moisture.

### Oxygen in Non-Mineral Matter

There being no satisfactory direct method for determining oxygen, it is computed by subtracting the sum of the percentages of hydrogen (p. 120), carbon (p. 120), nitrogen (p. 340), sulphur (p. 1112), water and ash from 100 per cent. The result so obtained is affected by all the errors incurred in the other determinations, and especially by the change in weight of the ash-forming constituents on ignition. Iron pyrites will absorb oxygen from the air and change to ferric oxide, increasing the weight of ash, and thereby causing a negative error in the oxygen, equivalent to three-eighths of the pyritic sulphur. Any calcium carbonate present will tend to absorb sulphur combined with the bituminous constituents. On the other hand, there is always a loss on ignition of "water of composition" from the clayey and shaley constituents, also carbon dioxide from carbonates, etc., which tend to compensate for the absorption of oxygen.<sup>2</sup>

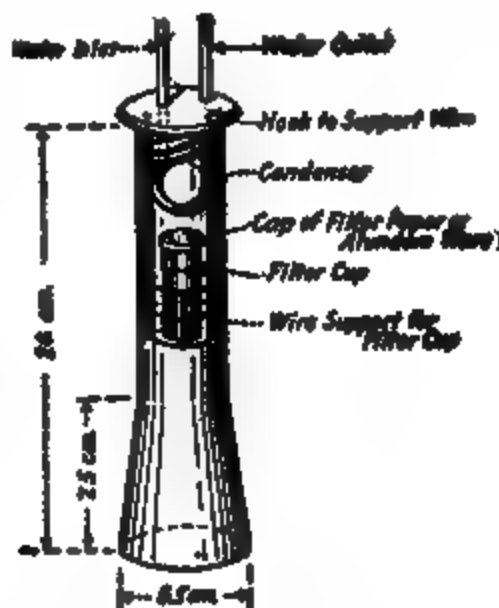
<sup>1</sup> "Methods for the Determination of Water in Petroleum and its Products," by I. C. Allen and W. A. Jacobs, Tech. Paper 25, Dept. of Interior, Bureau of Mines, Wash., D. C., 1912.

<sup>2</sup> "Standard Methods for Laboratory Sampling and Analysis of Coal" (Serial Designation: D 22-16), A. S. T. M. Standards, 1918, 679.

## Free Carbon in Tars

This represents an adaptation of the carbon disulphide method suitable for testing tars and pitches for the presence of non-mineral matter insoluble in hot toluol-benzol, which has been found the most satisfactory menstruum for this purpose.<sup>1</sup>

The apparatus used was devised by H. J. Cary-Curr and is illustrated in Fig. 159.



From A. S. T. A. Standards.

FIG. 159.—Cary-Curr Extraction Apparatus.

The filtering medium may consist either of a paper thimble or two thicknesses of Schleicher & Schuell's No. 575 hardened filter paper, 15 cm. in diameter, arranged in the shape of a cup by folding symmetrically around a stick 1 in. in diameter. It should be soaked in benzol to remove any grease, dried in an oven, desiccated and weighed.

Tars must be dehydrated before extracting, and pitches if sufficiently hard, ground to a fine powder. In testing materials containing more than 5 per cent of free carbon, 5 g. should be used, and 10 g. with smaller percentages. Weigh a suitable amount in a 100-cc. beaker and digest with 50 cc. c.p. toluol on a steam bath with constant stirring for not exceeding 30 minutes. Place the prepared filter paper in a carbon filter-tube and decant the toluol extract through it. Wash with hot c.p. toluol until the filtrate is clear, using a "policeman" unaffected by toluol for detaching any free carbon adhering to the beaker. Finally wash the filter with hot c.p. benzol, and after draining, cover it with a cap of filter paper or alundum ware, and extract it in the apparatus with c.p. benzol until the drippings become colorless. This will take at least 2 hours. The filter is then removed, the cap taken off, the paper dried in a steam oven, cooled in a desiccator and weighed. With pitches it is well to examine the free carbon for foreign matter, such as wood slivers, pieces of bagging, etc. If such foreign matter is present, the test should be rejected.

## Solid Paraffines

The following method does not give absolute figures, since it merely discloses the paraffine hydrocarbons which are solid at room temperature, without taking the liquid paraffines into consideration; nevertheless the results are of value for purposes of comparison.<sup>2</sup> Weigh 50 g. of the material in a tared 6-oz. glass retort, and slowly distil

<sup>1</sup> "Free Carbon, Its Nature and Determination in Tar Products," by J. M. Weiss, *J. Ind. Eng. Chem.*, 6, 279, 1914; "Some Effects of Certain Solvents on Tars in the 'Free Carbon' Determination," by G. S. Monroe and H. J. Broderick, *J. Ind. Eng. Chem.*, 9, 1100, 1917.

<sup>2</sup> "The Modern Asphalt Pavement," by Clifford Richardson, 2nd Edition, 558, 1908; "Untersuchung der Kohlenwasserstofföle und Fette," by D. Holde, Berlin, 45, 1913; "Laboratory Manual of Bituminous Materials," by Prevost Hubbard, N. Y., 100, 1916.

until nothing but a residue of coke remains. The distillation should take in the neighborhood of 45 minutes from the time the first drop comes over. The distillate is caught in an Erlenmeyer flask, and weighed. Either 5 or 10 g. of the well mixed distillate, depending upon the quantity of solid paraffines present in the crude material, are transferred into a large test tube and dissolved in 25 cc. of absolute ethyl ether and 25 cc. of absolute ethyl alcohol. A similar mixture containing 25 cc. each of ether and alcohol is made up, and this together with the oil solution is cooled separately to exactly 0° F. for  $\frac{1}{2}$  hour in a mixture of ice and salt (to which if necessary calcium chloride may be added). The oil solution is then rapidly filtered through a weighed Gooch crucible, similarly maintained at 0° F. by a jacket of ice and salt, and washed with 50 cc. of the cooled ether-alcohol mixture. A simple and convenient apparatus consists of an inverted bottle 6 in. in diameter, having the bottom cut off, and attached to the same rubber stopper which supports the funnel holding the Gooch crucible. The space between the bottle, the crucible, and the supporting funnel is packed with the ice and salt mixture. The Gooch crucible is then removed, the outside wiped clean, placed on a tared glass and dried in an oven at 80° C. until the last traces of ether and alcohol are evaporated. The residue is weighed, and the percentage of solid paraffines calculated in the original 50 g. of substance taken for analysis.

### Sulphonation Residue

The method of determining the sulphonation residue as proposed by Dean & Bateman,<sup>1</sup> consists in distilling sufficient of the material under examination by the flask method to obtain at least 10 cc. of distillate between 315 and 355° C. Exactly 10 cc. of this fraction are measured into a Babcock milk bottle, and 40 cc. of 37 normal sulphuric acid added, 10 cc. at a time. The bottle and its contents are shaken for 2 minutes after each addition, and when all the acid has been added, the bottle is kept at a constant temperature of 98–100° C. for one hour, during which it is shaken vigorously every 10 minutes. At the end of the hour, the bottle is removed, cooled, filled to the top of the graduations with ordinary sulphuric acid, and whirled for 5 minutes in a Babcock separator. The unsulphonated residue multiplied by 2 gives the per cent by volume directly (each graduation being equal to  $\frac{1}{200}$  of a cc.).

It is important that the acid should be of the proper strength. A mixture of fuming sulphuric acid and ordinary concentrated sulphuric acid should be prepared to contain exactly 80.07 per cent of  $\text{SO}_3$ , which constitutes 37 normal acid. If the sulphonation residue is dark in color, it should be treated with an excess of a 10 per cent sodium hydroxide solution, and if completely soluble in this reagent, the test is negative.

### Unsaponifiable and Saponifiable Matters

Certain bituminous substances, such as montan wax, rosin pitch, and fatty-acid pitch are often composed largely of saponifiable constituents. Others, including pine tar, pine-tar pitch, hardwood tar, hardwood-tar pitch, peat tar, lignite tar, bone tar, bone-tar pitch and others forms of fatty-acid pitches contain smaller percentages. This test is also used for gauging the uniformity of supply, and in the case of fatty-acid pitches, as a criterion of the quality.

The following procedure has been devised by the author for specifically examining bituminous materials or admixtures of bituminous materials with animal or vegetable oils and fats, since the customary methods do not adapt themselves especially well, due to the formation of troublesome emulsions. The bituminous material is first freed from insoluble constituents, including any mineral matter, by boiling with carbon disulphide under a reflux condenser, cooling and filtering through a Gooch crucible.

<sup>1</sup> "The Analysis and Grading of Creosotes," Forest Service Circular 112, Wash., D. C.; "Modification of the Sulphonation Test for Creosote," Forest Service Circular 191, Wash., D. C.; "Methods for Testing Coal Tar and Refined Tars, Oils and Pitches Derived Therefrom," by S. R. Church, J. Ind. Eng. Chem., 3, 233, 1911; 5, 196, 1913; "Paraffin Bodies in Coal Tar Creosote and their Bearing on Specifications," by S. R. Church and J. M. Weiss, J. Ind. Eng. Chem., 6, 396, 1914.

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The insoluble constituents are dried at 100° C. and weighed. Sufficient of the bituminous substance should be taken to yield approximately 5.0 g. of extract. The benzol solution is evaporated or distilled to 50 cc. and 50 cc. of the saponifying liquid added from a pipette. This should consist of a 10 per cent solution of caustic potash, prepared by dissolving 100 g. of anhydrous potash in 500 cc. of 95 per cent ethyl alcohol, and diluting to a litre with 90 per cent benzol. The liquid is allowed to stand overnight to permit any carbonate to settle, and the clear solution decanted. After the saponifying agent is added, the mixture is boiled under a reflux condenser, for  $\frac{1}{2}$ –1 hour, and the contents of the flask while still warm poured in a separatory funnel containing 150 cc. of boiling water and 25 cc. of a 10 per cent solution of potassium chloride. Add 250 cc. of benzol, agitate vigorously, and allow the funnel to rest quietly in a warm place until the solvent separates. If an emulsion forms which refuses to separate on standing, add 200 cc. more benzol and 100 cc. 95 per cent ethyl alcohol and stand in a warm place overnight. This will invariably effect a more or less complete separation of the solvent. From this point on the method is illustrated by the following tabular outline:

Saponify as described:

Draw off the soap solution as completely as possible.

Decant the benzol layer, leaving the intermediate layer in the separatory funnel.

Aqueous Soap Solution. Exhaust with 200 cc. portions of benzol.		Benzol Layer.	Intermediate Layer.
Aqueous Soap Solution.	Combined Benzol Extracts.		
	Combine and exhaust with 100 cc. portions of 50% alcohol.		
	Benzol Solution.	Combined Alcoholic Extracts.	
		Combine and exhaust with benzol.	
		Combined Benzol Extracts.	Alcoholic Soap Solution.
	Combine, evaporate to a small bulk, complete the evaporation at 100° C., cool and weigh the <i>Unsaponifiable Constituents</i> .		
	Combine		

Transpose with dilute hydrochloric acid, warm and exhaust with benzol. Separate the aqueous solution containing the glycerol and mineral salts. Evaporate the combined benzol extracts to a small bulk, and then complete the evaporation of solvent at 100° C. Cool and weigh. Weight equals the *free acids derived from the saponifiable constituents*.

In the case of bituminous materials that are more or less completely saponifiable, the intermediate layer is apt to be absent. In this case the process will simplify itself considerably. The foregoing procedure will separate the unsaponifiable constituents in practically an ash-free state.

### Diazo Reaction

This test is used for identifying bituminous substances carrying phenols, including wood tar and wood-tar pitch, oil-gas- and water-gas-tars and pitches, shale tar, peat- and lignite-tars and pitches, bone tar, bone-tar pitch and the various coal-tar pitches.

This reaction was devised by E. Graefe.<sup>1</sup> It is carried out by boiling 2 g. of the

<sup>1</sup> "Distinction between Lignite Pitch and other Pitches," Chem. Zeit., 30, 298, 1906; Marcusson and Eickmann, Chem. Zeit., 32, 965, 1908.

bituminous substance with 20 cc. N. aqueous caustic soda, for approximately 5 minutes. After cooling, the liquid is filtered. If the filtrate is dark colored, it may be lightened by adding finely pulverized "salt." It is then cooled in ice, and a few drops of freshly prepared diazobenzochloride solution (prepared by treating anilin with hydrochloric acid and sodium nitrite) added. If phenols are present a red coloration will result, sometimes accompanied by a reddish precipitate.

Assuming that the bituminous substance gives the diazo reaction, the question will often arise whether the product is a straight-distilled pitch, or an asphalt "cut-back" with a high boiling-point distillate containing phenolic bodies, derived from coal tar, lignite tar, etc. Marcumson has worked out a method applicable under these circumstances,<sup>1</sup> which consists in dissolving 10 g. of the bituminous substance in 15 cc. of benzol, and pouring the solution into 200 cc. of 88° petroleum naphtha. The resulting precipitate is washed with petroleum naphtha and dried. It is then boiled for 15 minutes with N/2 alcoholic caustic potash under a reflux condenser to extract the phenols. The liquid is cooled and filtered, the alcohol evaporated, and the residue dissolved in water. Sodium chloride is added to clarify the liquid and remove any substances imparting a dark color, the solution is filtered and the filtrate treated for the diazo test described above. If a straight distilled pitch containing phenols is present, a positive reaction will be obtained. If the original substance gives the diazo test, but the residue treated in the above way does not, then the admixture of high boiling-point oils containing phenolic bodies with a substance free from phenols (e.g., asphalt, etc.) is established. The presence of 10 per cent asphaltic substances may be detected.

Where bituminous substances contain calcium carbonate, the phenolic bodies present combine with the lime, forming insoluble calcium phenolate which yields but a faint diazo reaction. However, on treating such substances with a solvent in the presence of hydrochloric acid, the calcium phenolate is decomposed, and the diazo reaction becomes much more delicate.

### Anthraquinone Reaction

The anthraquinone reaction is used for detecting anthracene in tar products produced at high temperatures, including oil-gas-tar and pitch, water-gas-tar and pitch, and the various coal-tar pitches.

The tar or pitch is first subjected to distillation in accordance with the retort method, the offtake and condensing tube being kept warm to prevent the accumulation of any solid distillate. The distillate passing over between 270 and 355° C. is caught separately and examined for anthracene in the following manner. The fraction is heated until it is thoroughly fluid to secure a uniform sample, and 5 g. weighed out, while hot. After cooling, 10 cc. of absolute ethyl alcohol are added, the solids allowed to crystallize and the liquid decanted. The solid substances containing the anthracene are dried on a water bath, transferred to a 500-cc. flask connected with a return condenser, 45 cc. of glacial acetic acid added, and the contents boiled for 2 hours. The following mixture is then added drop by drop through a separatory funnel, viz: 15 g. of anhydrous chromic acid dissolved in 10 cc. of glacial acetic acid, and 10 cc. of water. The boiling is continued for another 2 hours, the flask cooled, and 400 cc. cold water added. This treatment oxidizes the anthracene to anthraquinone, which on cooling separates as a solid mass. This is filtered, washed with hot water, then with a hot 1 per cent solution of caustic soda and again with hot water. The residue of anthraquinone is then dried and its weight multiplied by 0.856 to obtain the corresponding weight of anthracene. From 0.25 to 0.75 per cent of anthracene is found in coal tars, and a corresponding larger percentage in coal-tar pitches.

A color reaction for establishing the presence of anthracene consists in boiling the crystals of anthraquinone with zinc dust and caustic soda solution, whereupon an intense red colored solution is obtained, which on filtering becomes decolorized by air.

<sup>1</sup> Chem. Rev. Fett-und Harz-Ind., 18, 47, 1911.

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TABLE III.—SYNOPTICAL TABLE OF THE MOST IMPORTANT

	Fracture	Streak	Sp. gr. at 77° F. (Non-mineral Matter)	Consistency at 77° F.	Susceptibility Factor	Fusibility °F. (K. and N. Method)
Non-asphaltic petroleum .....	.....	.....	0.75-0.90	Liquid	.....	<60
Mixed-base petroleum .....	.....	.....	0.80-0.95	Liquid	.....	<60
Asphaltic petroleum .....	.....	.....	0.85-1.00	Liquid	.....	<60
Ozokerite .....	Conch. to H	Wh. to Yel	0.85-1.00	100-110	>80	140-200
Montan wax .....	Conch.	Yel.	0.90-1.00	>100	>100	170-200
Paraffine wax .....	Conch. to H	Wh.	0.85-0.95	15-80	>100	100-150
Native asphalt (contg. less than 10% mineral matter) .....	Variable	Bn. to Bk.	0.95-1.12	0- >100	15- >100	80-325
Native asphalt (contg. greater than 10% mineral matter) .....	Variable	Bn. to Bk.	0.95-1.15	5- >100	30- >100	80-350
Residual oils .....	.....	.....	0.85-1.05	0-7	.....	0-80
Blown petroleum asphalts .....	Variable	Bn. to Bk.	0.90-1.07	2-30	8-40	80-400
Residual asphalts .....	Conch.	Bk.	1.00-1.17	5-100	40-60	80-225
Sludge asphalts .....	Conch.	Bk.	1.05-1.20	5-100	40-60	80-225
Wurtzilite asphalt .....	Conch.	Bn. to Bk.	1.04-1.07	20-50	30-40	150-300
Gilsonite .....	Conch.	Bn.	1.05-1.10	90-120	>100	250-375
Glance pitch .....	Conch. to H	Bk.	1.10-1.15	90-120	>100	250-350
Grahamite .....	Conch. to H	Bk.	1.15-1.20	>150	>100	350-600
Elastrite .....	.....	Bn.	0.90-1.05	Rubbery	.....	Inf.
Wurtzilite .....	Conch. to H	Bn.	1.05-1.07	>150	.....	Inf.
Albertite .....	Conch. to H	Bn. to Bk.	1.07-1.10	>150	.....	Inf.
Impsonite .....	Hackly	Bk.	1.10-1.25	>150	.....	Inf.
Asphaltic pyrobituminous shales .....	Conch.	Var.	1.50-1.75	>150	.....	Inf.
Peat (dry) .....	Variable	Bn.	0.15-1.05	>150	.....	Inf.
Lignite (dry) .....	Variable	Bn.	1.00-1.25	>150	.....	Inf.
Bituminous coal .....	Hackly	Bn. to Bk.	1.20-1.40	>150	.....	Inf.
Anthracite coal .....	Conch. to H	Bk.	1.30-1.60	>150	.....	Inf.
Non-asphaltic pyrobituminous shales .....	Conch.	Var.	1.30-1.75	>150	.....	Inf.
Wax tailings .....	.....	Yel.	1.00-1.10	5-20	20-40	60-100
Oil-gas tar .....	.....	.....	0.95-1.10	0	.....	<0-20
Oil-gas-tar pitch .....	Conch.	Bk.	1.15-1.30	10-100	>100	80-275
Water-gas tar .....	.....	.....	1.05-1.15	0	.....	<0-10
Water-gas-tar pitch .....	Conch.	Bk.	1.10-1.20	10-100	>100	80-275
Pine tar .....	.....	.....	1.05-1.10	0	.....	0-50
Pine-tar pitch .....	Conch.	Bn.	1.10-1.15	10-100	>100	100-200
Hardwood tar .....	.....	.....	1.10-1.20	0	.....	0-20
Hardwood-tar pitch .....	Conch.	Bn. to Bk.	1.20-1.30	10-100	>100	100-200
Rosin pitch .....	Conch.	Yel. to Bn.	1.08-1.15	50-100	>100	120-200
Peat tar .....	.....	.....	0.90-1.05	0	.....	40-80
Peat-tar pitch .....	Conch.	Bn. to Bk.	1.05-1.15	10-100	>100	100-250
Lignite tar .....	.....	.....	0.85-1.05	0	.....	80-90
Lignite-tar pitch .....	Conch.	Bk.	1.05-1.20	10-100	>100	100-250
Shale tar .....	.....	.....	0.85-0.95	0	.....	60-90
Gas-works coal tar .....	.....	.....	1.15-1.30	0	.....	<0-25
Gas-works coal-tar pitch .....	Conch.	Bk.	1.15-1.40	10-100	>100	80-300
Coke-oven coal tar .....	.....	.....	1.10-1.30	0	.....	<0-25
Coke-oven coal-tar pitch .....	Conch.	Bk.	1.20-1.25	10-100	>100	80-300
Blast-furnace coal tar .....	.....	.....	1.15-1.30	0	.....	<0-25
Blast-furnace coal-tar pitch .....	Conch.	Bk.	1.20-1.30	10-100	>100	80-300
Producer-gas coal tar .....	.....	.....	1.15-1.30	0	.....	<0-25
Producer-gas coal-tar pitch .....	Conch.	Bk.	1.20-1.35	10-100	>100	80-300
Bone tar .....	.....	.....	0.95-1.05	0	.....	<0-10
Bone-tar pitch .....	Conch.	Bk.	1.10-1.20	10-100	75-100	80-225
Fatty-acid pitch .....	Variable	Yel. to Bk.	0.90-1.10	0-40	8-40	35-225

Table III gives the limiting values of the tests ordinarily used for distinguishing the individual bituminous substances.

## DISTINGUISHING CHARACTERISTICS OF BITUMINOUS SUBSTANCES

Fixed Carbon	Solubility in Carbon Disulphide	Non-mineral Matter Insoluble	Mineral Matter	Carburene	Soluble in 88° Naphtha	Oxygen in Non-mineral Matter	Paraffine	Sulphonation Residue	Saponifiable Matter	Diaz Reaction	Anthraquinone Reaction
% 1-2 2-5 5-10	98-100 95-100 90-100	0-1 0-1 0-1	0-2 0-2 0-2	0-1 0-1 0-1	95-100 95-100 90-100	0-2 0-2 0-5	10-25 1-10 0-Tr.	85-95 85-95 80-95	0-2 0-2 0-5	No No No	No No No
1-10 2-10 0-2	95-100 98-100 99-100	0-1 0-2 0-1	0-5 0-2 0-1	0-3 0-2 0	75-95 80-100 99-100	0-2 3-6 0-Tr.	50-90 0-10 95-100	90-100 0-10 95-100	0-2 0-2 0	No No No	No No No
1-25 5-25 2-10 5-20 5-40 5-30 5-25	80-98 Tr.-90 95-100 93-100 85-100 95-100 95-100	0-25 0-1 0-6 0-15 0-1 0-1 0-1	0-10 10-95 0-1 0-1 0-1 0-1 Tr.-2	0-5 0-5 0-1 0-10 0-30 0-15 0-2	85-95 Tr.-85 80-99 80-99 85-95 85-95 85-95	0-2 0-2 0-3 2-5 0-2 3-7 0-2	0-5 0-5 0-15 0-10 0-5 0-1 0-Tr.	90-100 90-100 90-100 90-100 90-100 80-95 85-95	0-2 0-2 Tr.-5 Tr.-2 0-2 0-2 Tr.	No No No No No No No	No No No No No No No
10-20 20-30 30-55	98-100 95-100 45-100	0-1 0-1 0-5	Tr.-1 Tr.-5 Tr.-50	0-1 0-1 0-80	40-60 20-30 Tr.-50	0-2 0-2 0-2	0-Tr. 0-Tr. 0-Tr.	85-95 85-95 80-95	Tr. Tr. Tr.	No No No	No No No
2-5 5-25 25-50 50-85 2-25*	10-20 5-10 2-10 1-6 Tr.-3	70-90 80-95 90-99 90-99 15-70	Tr.-10 Tr.-10 Tr.-10 Tr.-10 30-85	Tr.-2 Tr.-2 Tr.-2 Tr.-2 0-Tr.	5-10 Tr.-2 Tr.-2 Tr.-2 0-Tr.	1-5 0-2 0-3 0-3 0-3	0-Tr. 0-Tr. 0-Tr. 0-Tr. Tr.-3	80-90 90-98 90-98 90-98 80-95	Tr.-15 Tr. Tr. Tr. Tr.	No No No No No	No No No No No
15-35 25-30 35-75 60-90 20-45*	1-1 2-15 1-2 0-1 0-1	15-90 65-98 75-98 75-98 15-70	2-80 2-25 2-25 2-25 30-85	0-2 0-1 0-1 0 0	0-5 5-10 0-1 0 0-1	26-44 15-28 3-18 1-5 3-15	..... ..... ..... ..... .....	..... ..... ..... ..... .....	Tr.-15 Tr.-5 Tr.-1 0 Tr.-2	No No No No No	No No No No No
2-8 10-25 20-30 10-20 25-40	95-100 98-100 85-98 95-100 85-98	0-2 0-2 2-15 0-1 2-15	0-Tr. 0-1 0-1 0-1 0-1	0-Tr. 0-2 0-2 0-2 2-15	95-100 80-85 85-85 85-78 50-80	0-2 1-2 0-2 1-2 0-2	Tr.-5 0-5 0-5 0-5 0-5	90-100 80-90 80-90 0-15 0-15	Tr. Tr. 0-1 Tr.-2 0-1	No Yes Yes Yes Yes	Yes Yes Yes Yes Yes
5-15 10-25 5-20 15-35 15-35	95-100 40-95 95-100 30-95 95-100	0-2 2-60 0-5 5-70 0-2	0-1 0-1 0-1 0-1 0-1	0-1 0-5 0-2 2-10 0-5	85-95 25-80 50-90 15-60 85-95	5-10 2-8 2-10 1-5 5-10	0 0 0 0 0	Tr.-5 Tr.-3 Tr.-5 Tr.-5 Tr.-5	10-50 10-40 5-25 5-25 25-95	Yes Yes Yes Yes Yes	No No No No No
5-15 15-30 5-20 10-40 5-10	98-100 95-99 98-100 95-99 95-100	0-2 0-5 0-1 0-2 0-2	0-1 0-1 0-1 0-1 0-1	0-2 0-5 0-2 0-5 0-2	95-100 85-95 85-100 75-95 95-100	5-15 2-8 5-10 2-5 1-5	5-15 2-5 10-25 1-5 5-15	5-15 5-10 10-20 5-15 15-35	5-15 0-5 5-20 0-5 0-2	Yes Yes Yes Yes Yes	No No No No No
15-40 30-45 15-40 20-45 5-25 10-30 15-35 25-45	80-95 55-90 80-97 60-85 65-80 50-75 75-90 80-85	5-40 10-45 3-20 15-40 10-25 15-35 10-25 15-40	0-1 0-1 0-1 0-1 10-15 10-20 0-2 0-2	0-2 0-2 0-2 2-10 0-2 2-10 0-2 2-10	85-95 20-40 20-40 10-30 15-35 5-25 20-40 10-30	1-3 Tr.-2 1-3 Tr.-2 1-3 Tr.-2 1-3 Tr.-2	0 0 0 0 0 0 0 0	0-5 0-5 0-5 0-5 5-20 5-20 0-5 0-5	2-5 Tr.-1 2-5 Tr.-1 2-5 Tr.-1 2-5 Tr.-1	Yes Yes Yes Yes Yes Yes Yes Yes	Yes Yes Yes Yes Yes Yes Yes Yes
5-15 15-25 5-35	95-100 85-95 95-100	0-5 1-15 0-5	0-Tr. 0-Tr. 0-5	0-2 0-10 0-5	95-100 75-95 85-100	2-8 0-2 2-10	0 Tr. Tr.	0-5 0-5 0-5	5-40 2-25 5-98	Yes Yes No	No No No

\* Calculated on mineral-free basis.



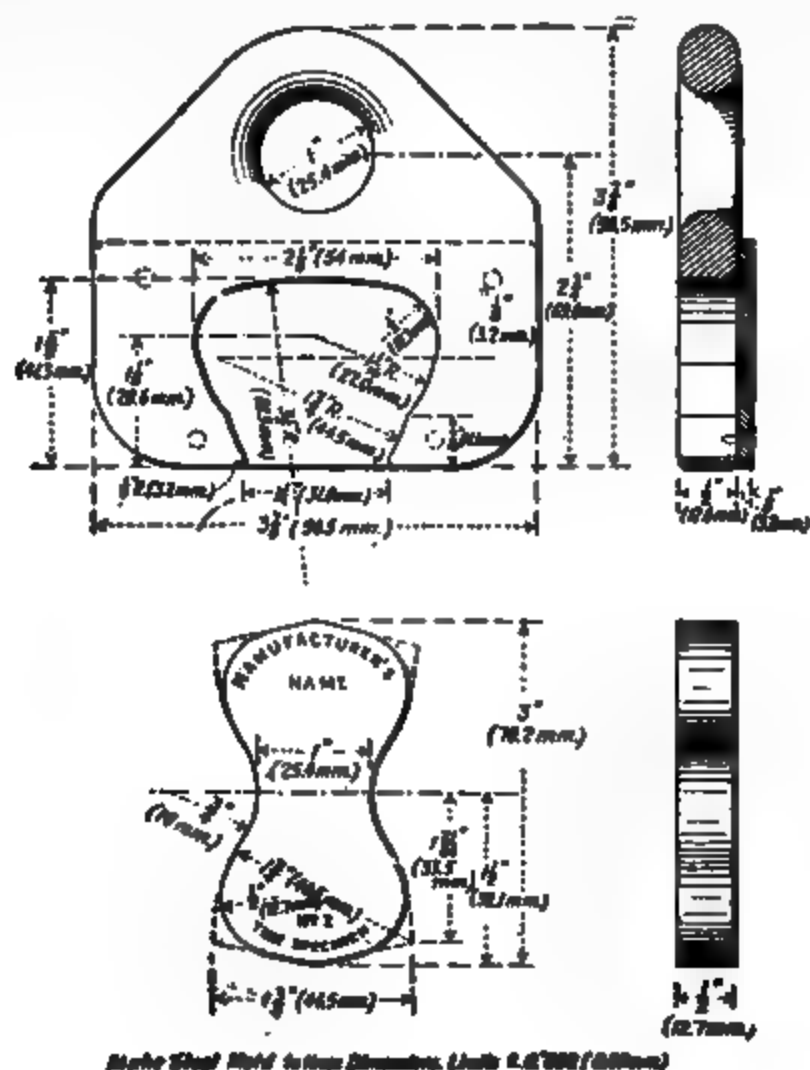
## PART II

## EXAMINATION OF BITUMINIZED MINERAL AGGREGATES

Products falling into this class include native and artificial mixtures of bituminous matter with mineral aggregates, viz.: bituminous macadam pavements, bituminous concrete pavements, sheet asphalt pavements, asphalt block pavements, asphalt mastic floorings, bituminous expansion joints (containing mineral matter but not felt), pipe-sealing compounds, moulding compositions and products used for electrical insulation.

## PHYSICAL TESTS OF FINISHED PRODUCT

**Tensile Strength.** The following tentative test has been proposed for moulded insulating materials,<sup>1</sup> but may also be adapted to testing the surface course of sheet asphalt pavements, asphalt mastic floorings, expansion joints (not containing fabric), pipe-sealing compounds, etc. The specimen is cast under pressure to obtain the greatest possible density, in a hardened and ground steel mould of the dimensions shown in Fig. 160, then immersed in distilled water for 48 hours at 77° F., removed, wiped



From A. S. T. M. Tent. Standards.

FIG. 160.—Mould for Ascertaining the Tensile Strength of Bituminized Aggregates.

dry and pulled apart on any standard testing machine in air at 77° F., at a speed that will enable the beam to be well balanced. The results of the test shall be reported in the following order, viz.: the breaking load in kilograms or pounds; the thickness in centimeters or inches as measured by a micrometer at the point of fracture; the ultimate tensile strength in kilograms per square centimeter or in pounds per square inch as calculated from the actual area of the specimen at the point of fracture; the speed in

<sup>1</sup> "Standard Tests for Molded Insulating Materials" (Serial Designation: D 48-17 T), Proc. Am. Soc. Testing Materials, 20. Part I, 776, 1920.

centimeters or inches per minute at which the jaws travel during the test. Three such tests should be averaged.

**Compressive Strength.** This test has likewise been proposed for moulded insulating materials,<sup>1</sup> and is adapted to all bituminized mineral aggregates in which the particles do not measure over  $\frac{1}{2}$  in. in diameter. A 1-in. cube is moulded under pressure in a hardened steel mould to attain the greatest possible density, and immersed in distilled water at 77° F. for 48 hours. Wipe the surface dry and place sheets of lead  $\frac{1}{8}$  in. thick both above and below the specimen to adjust irregularities. Any standard testing machine may be used, and the load shall be applied at such a rate of speed as will permit the beam to be kept well balanced. The results of the test shall be reported as follows, viz.: the dimensions of the specimen in millimeters or inches; the breaking load in kilograms or pounds at the first sign of failure; the average ultimate compressive strength in kilograms per square centimeter or pounds per square inch, calculated from the measured area of the specimen before the load is applied; the speed in centimeters or inches per minute at which the jaws travel during the test. Three such tests are averaged.

**Impact Test.** This test was originally devised by L. W. Page for testing the toughness of rock for road building,<sup>2</sup> having since been adapted by Richardson for testing bituminous aggregates.<sup>3</sup> The bituminous mixture is heated to the lowest possible temperature that will permit it being manipulated, and formed by compression into a cylinder 25 mm. high by 24–25 mm. in diameter, the ends of which shall be plane surfaces at right angles of its axis. The hot bituminous mixture is compressed in a hollow cylindrical steel mould, 24–25 mm. in diameter by 50 mm. long, having an accurately fitting steel plunger. The mould is loosely filled with the hot bituminous mixture and compressed with the plunger by sharp blows of a heavy hammer from the top and bottom respectively, until it is thoroughly compacted. The cylinder of bituminous material is then knocked from the mould and sawed off or ground down until it measures exactly 25 mm. high. The density of the specimen should be noted and reported. It shall be maintained in water at 77° F. for 48 hours, wiped dry, and tested in air at a temperature of 77° F. on any form of impact machine which will comply with the following essentials:

(a) A cast-iron anvil weighing not less than 50 kg. firmly fixed upon a solid foundation.

(b) A hammer weighing 2 kg. arranged to fall freely between suitable guides.

(c) A plunger of hardened steel weighing 1 kg. arranged to slide freely in a vertical direction in a sleeve, the lower end of the plunger being spherical, with a radius of exactly 1 cm.

(d) Means for raising the hammer and dropping it upon the plunger from any specified height from 1 to not less than 75 cm.

(e) Means for holding the cylindrical test-specimen securely on the anvil without rigid lateral support, and under the plunger in such a way that the centre of its upper surface shall, throughout the test, be tangent to the spherical end of the plunger at its lowest point.

The test shall consist of a 1 cm. fall of the hammer for the first blow; a 2 cm. fall for the second blow; and an increase of 1 cm. for each succeeding blow, until failure of the test specimen occurs. The number of blows required to shatter the test-piece is taken to represent the toughness, three such tests being averaged. Tests are performed at three temperatures, viz.: 32° F., 77° F. and 115° F.

**Distortion under Heat.** This test is applicable to bituminized mineral aggregates whose particles do not exceed  $\frac{1}{2}$  in. in diameter. The material shall be compressed to the greatest possible density in a hardened steel mould, ground so its internal dimensions will measure  $\frac{1}{2}$  in. by  $\frac{1}{2}$  in. by 5 in.<sup>4</sup>

<sup>1</sup> "Tentative Tests for Molded Insulating Materials" (Serial Designation: D 48-17 T), Proc. Am. Soc. Testing Materials, 20, Part I, 777, 1920.

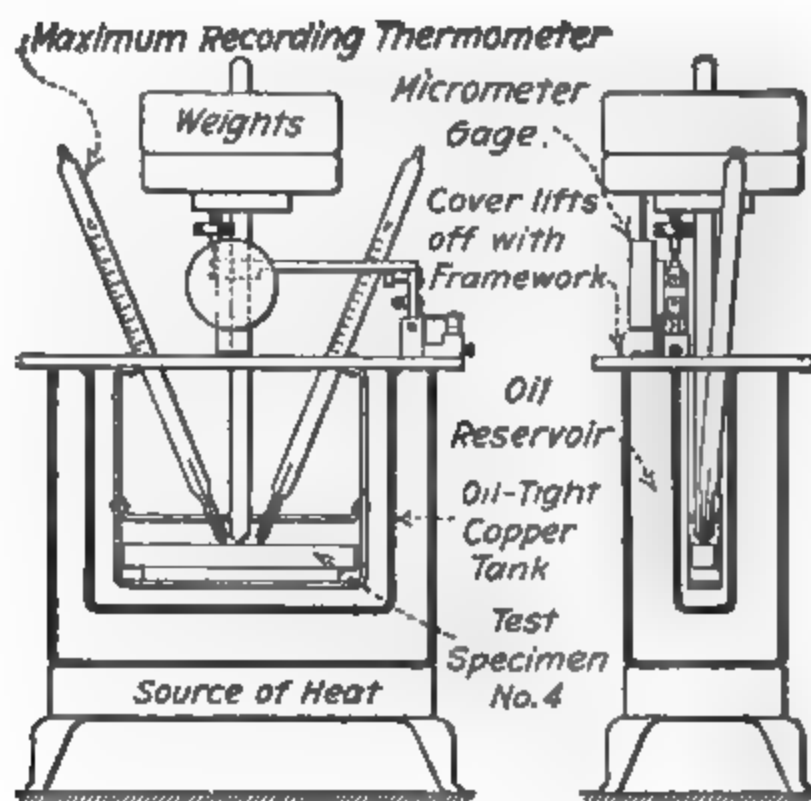
<sup>2</sup> Bulletin No. 79, Bureau of Chem., U. S. Dept. of Agr., Wash., D. C.; Bulletin No. 44, Office of Public Roads, U. S. Dept. of Agr., Wash., D. C., June 10, 1912.

<sup>3</sup> "The Modern Asphalt Pavements," 2nd Edition, 1908, pp. 428 and 585.

<sup>4</sup> "Tentative Tests for Molded Insulating Materials" (Serial Designation: D 48-17 T), Proc. Am. Soc. Testing Materials, 17, Part I, 703, 1918.

## 1330 EXAMINATION OF BITUMINOUS SUBSTANCES

The apparatus used for this purpose is illustrated in Fig. 161. The specimen



From A. S. T. M. Tent. Standards.

FIG. 161.—Apparatus for Recording Distortion of Bituminized Aggregates under Heat.

should rest on steel supports 100 mm. apart, and the load applied on top of the specimen vertically and midway between the supports, as in the transverse strength test. The machine shall be arranged to apply two different loads, viz.: 2.5 kg. and 5.0 kg. The specimen is placed in an air bath surrounded by an oil bath, the temperature of which is increased at a rate of exactly 1° F. per minute. The deflection of the specimen at its center between the supports is measured on a scale in millimeters or mils. The distortion point shall be considered the temperature at which the specimen has deflected 10 mils. The results of the test are reported as follows, viz.: the distortion point in degrees F; the time required for the specimen to deflect 10 mils starting at 77° F.; curves are plotted, showing the minutes horizontally, and the corresponding deflection, also the temperature at given intervals vertically.

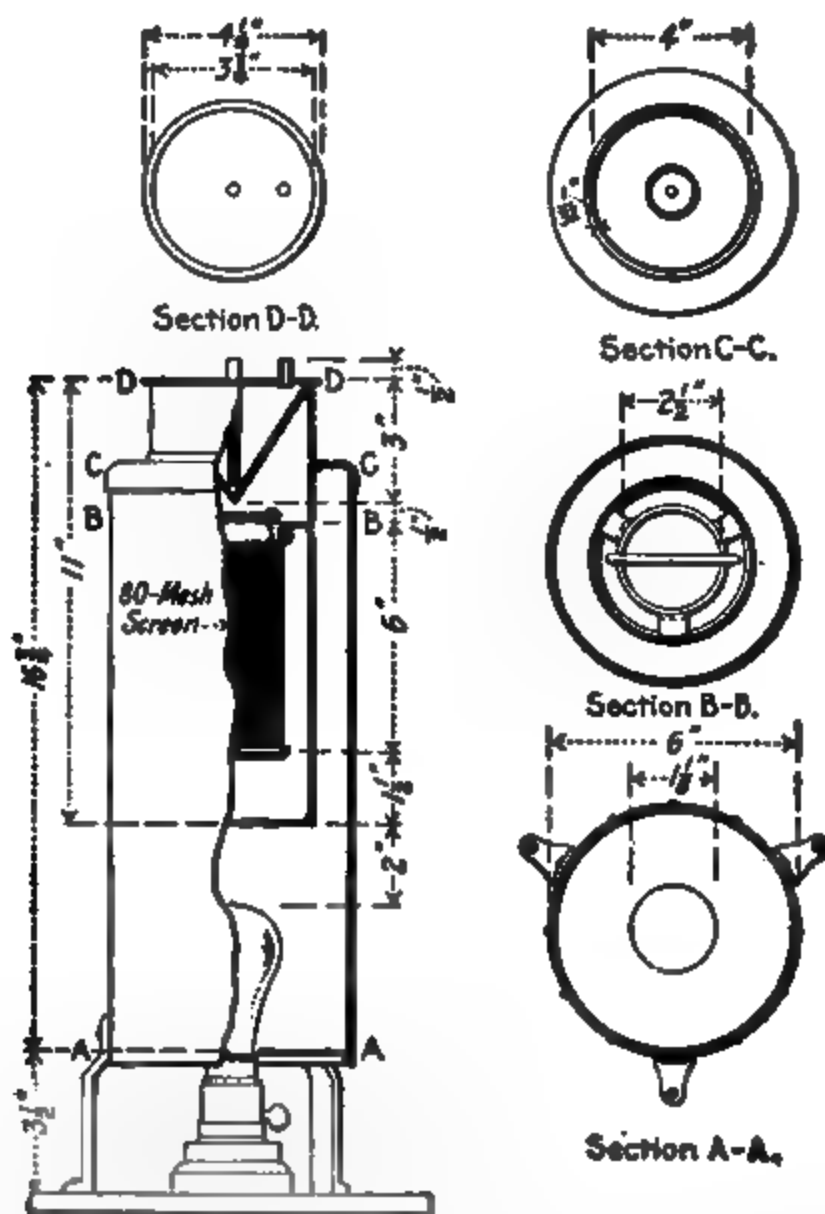
## SEPARATION OF FINISHED PRODUCT INTO ITS COMPONENT PARTS

### Separation of the Bituminous Matter and Mineral Aggregate

Bituminized aggregates are separated into their bituminous and mineral components for the combined purposes of ascertaining the percentage and nature of the mineral constituents, and for examining the physical and chemical characteristics of the bituminous binder, with the object of its identification or duplication. Two methods are used, including the hot extraction process devised by Forrest, and the centrifugal extraction method.

*Forrest's Hot Extraction Method.* The bituminous mixture should first be warmed until it may be broken apart without fracturing the mineral particles. The extraction

is performed in an apparatus illustrated in Fig. 162, consisting of a cylindrical brass



From A. S. T. M. Proc.

FIG. 162.—Forrest's Hot-extraction Apparatus.

jacket surrounding an incandescent-light bulb to supply the necessary heat, and enclosing a brass vessel for holding the solvent, which in turn carries a cylindrical basket composed of 80 mesh-wire cloth for retaining the sample. Cold water is circulated through the inverted conical condenser, which also serves to cover the apparatus. Weigh out 500 g. of material if the mineral particles are coarser than  $\frac{1}{2}$  in., or 300 g. if they are finer than  $\frac{1}{2}$  in. Place it in the basket and cover with a pad of cotton or felt  $\frac{1}{4}$ – $\frac{1}{2}$  in. thick. Pour 175–200 cc. of carbon disulphide into the inner vessel, insert the cover and start the extraction by turning on the incandescent light. The extraction is usually completed in 3 hours' time, whereupon the apparatus is cooled, the basket containing the mineral aggregate removed, dried in an oven and weighed. Any fine mineral particles passing through the 80-mesh sieve constituting the basket are recovered by filtering the extract through a weighed asbestos Gooch filter, washed clean with carbon disulphide, dried and weighed. This method is used where the bituminous matter is to be separated in a pure state for further examination. An alternate method consists in measuring the extract in a glass graduate, thoroughly agitating it and pouring an aliquot portion into a tared crucible or dish, evaporating the solvent, burning the residue and igniting to ash. The fine mineral matter present in the entire extract may be calculated from the ash derived from the portion ignited. The total should be added to the coarser mineral aggregate previously separated, to arrive at the percentage present.<sup>1</sup>

<sup>1</sup> "Extractor for Bituminous Paving Mixtures," by C. N. Forrest, Proc. Am. Soc. Testing Materials, 13, 1069, 1913.

*Centrifugal Method.* The most efficient apparatus of this type was designed by C. S. Reeve,<sup>1</sup> as illustrated in Fig. 163. It consists of a 1/5 h.p. vertical motor a,

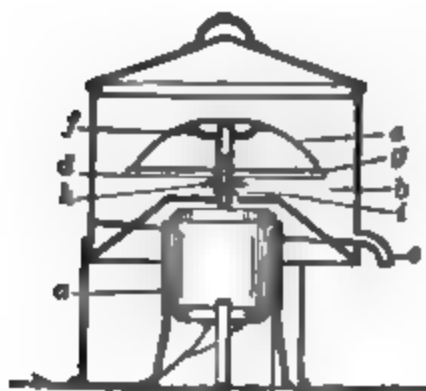


FIG. 163.—Centrifugal Extractor.

capable of making 1100 revolutions per minute at 110 volts, with either direct or alternating current. Its shaft projects into a cylindrical copper vessel b, having a concave bottom and draining into the spout c. A circular brass plate d, 9½ in. in diameter supports an inverted iron bowl e, 8½ in. in diameter by 2½ in. high, having a 2 in. circular hole at the top. A brass cup f is fastened to the inner side of the bowl, having a circle of ¼ in. holes for the admission of solvent, and terminating in a hollow axle which fits snugly through a hole in the center of the brass plate d. A felt ring g, ¼ in. wide and about 0.000 in. thick (cut from No. 80 roofing felt) is firmly pressed against the bowl by the milled nut h for which the hollow axle is suitably threaded. The axle in turn fits snugly over the shaft of the motor, to which it is secured by a slot and cross-pin.

Weigh 300–500 g. of the bituminous mixture, broken up as previously described, into the bowl e, place the felt ring on the rim of the plate d, and bolt them together with the nut i. After assembling the apparatus, pour 150 cc. of carbon disulphide into the bowl through the small holes, place the cover over the copper box b, and slowly start the motor, gradually increasing its speed until the carbon disulphide extract flows in a thin stream from the spout c into an empty flask underneath. When the first charge has drained, the motor is stopped, fresh carbon disulphide added, and the operation repeated 4 to 6 times until the extract runs clear. The bowl is then removed, inverted, the nut unscrewed, and any carbon disulphide retained by the mineral matter allowed to evaporate spontaneously. The mineral matter is then dried and weighed. It is well to filter the extract through a Gooch crucible to recover any mineral matter which may have worked its way through the felt ring, adding same to the balance of the mineral matter.

*Recovery of Extracted Bituminous Matter.* From the weight of the extracted mineral matter, calculate the bituminous matter by difference, and evaporate the carbon disulphide extract to exactly this weight. This may be conveniently performed by distilling and condensing most of the carbon disulphide over an incandescent light or an electric stove. The concentrated solution is transferred to a tared dish, evaporated dry on a steam bath, and the last traces of solvent removed in an oven at 105° C. until the residue attains the calculated weight. Due allowance should be made for the fact that any non-mineral matter insoluble in carbon disulphide will be retained mechanically by the extracted mineral matter, which with asphaltic products is relatively unimportant, but will amount to a considerable item in the case of tar products.

*Recovered Mineral Aggregate.* The presence of any non-mineral matter insoluble in carbon disulphide will be revealed by the discoloration of the mineral particles. In this case, the weight of the latter should be corrected by igniting it until all carbonaceous matter is destroyed, and then reweighing.

#### Examination of Separated Bituminous Matter

This is subjected to the tests embodied in Part I.

<sup>1</sup> "Laboratory Manual of Bituminous Materials," 1st Edition, N. Y., 1916, p. 108.

### Examination of Separated Mineral Matter

This will include any uncombined mineral matter as well as any colloidal mineral particles retained by an asbestos Gooch filter. It may be examined further as follows:

**Granularmetric Analysis.** The methods which follow have been standardised by the American Society for Testing Materials<sup>1</sup> for mineral aggregates used in connection with highways. The following three methods have been adopted:

**For Sand or Other Fine Highway Material.** The method consists of: (1) drying at not over 230° F. to a constant weight a sample weighing 50 g.; (2) passing the sample through each of the following mesh sieves.

Mesh Designation	Actual Mesh	Opening	Wire Diameter	Permissible Variations	
				Mesh	Diameter
10.....	3.9 cm.	2.00 mm.	0.56 mm.	±0.04	±0.05
	9.9 in.	0.079 in.	0.022 in.	±0.1	±0.002
20.....	8 cm.	0.85 mm.	0.40 mm.	±0.2	±0.015
	20.3 in.	0.0335 in.	0.0157 in.	±0.5	±0.0006
30.....	12 cm.	0.50 mm.	0.33 mm.	±0.4	±0.012
	30.5 in.	0.0197 in.	0.0130 in.	±1.0	±0.0005
40.....	16 cm.	0.36 mm.	0.26 mm.	±0.6	±0.010
	40.6 in.	0.0142 in.	0.0102 in.	±1.5	±0.0004
50.....	20 cm.	0.29 mm.	0.21 mm.	±0.8	±0.010
	50.8 in.	0.0114 in.	0.0083 in.	±2	±0.0004
80.....	31 cm.	0.17 mm.	0.15 mm.	±1	±0.008
	78.7 in.	0.0067 in.	0.0059 in.	±3	±0.0003
100.....	39 cm.	0.14 mm.	0.116 mm.	±1	±0.008
	99.1 in.	0.0055 in.	0.0046 in.	±3	±0.0003
200.....	79 cm.	0.074 mm.	0.053 mm.	±3	±0.005
	200.7 in.	0.0029 in.	0.0021 in.	±8	±0.0002

The order in which the sieves are to be used in the process of sifting is immaterial and shall be left optional; but in reporting results, the order in which the sieves have been used shall be stated; (3) determining the percentage by weight retained on each sieve, the sifting being continued until less than 1 per cent of the weight retained shall pass through the sieve during the last minute of sifting; and (4) recording the mechanical analysis in the following manner:

Passing 200-mesh sieve.....	%
Passing 100-mesh sieve and retained on a 200-mesh sieve...	%
Passing 80-mesh sieve and retained on a 100-mesh sieve...	%
Passing 50-mesh sieve and retained on a 80-mesh sieve...	%
.....	%
Total.....	100.00%

<sup>1</sup>"Standard Method for Making a Mechanical Analysis of Sand or Other Fine Highway Material, Except for Fine Aggregates Used in Cement Concrete" (Serial Designation: D 7-18); "Standard Method for Making a Mechanical Analysis of Broken Stone or Broken Slag, Except for Aggregates Used in Cement Concrete" (Serial Designation: D 18-18); "Standard Method for Making a Mechanical Analysis of Mixtures of Sand or Other Fine Material with Broken Stone or Broken Slag, Except for Aggregates Used in Cement Concrete" (Serial Designation: D 19-18), A. S. T. M. Standards, Adopted in 1918, 663, 665 and 666.

## 1334 EXAMINATION OF BITUMINOUS SUBSTANCES

**For Broken Stone or Broken Slag.** The method shall consist of: (1) drying at not over 230° F. to a constant weight a sample weighing in pounds 6 times the diameter in inches of the largest holes required; (2) passing the sample through such of the following size screens having circular openings as are required or called for by the specifications, screens to be used in the order named: 3½, 3, 2½, 2, 1½, 1¼, 1, ¾, ½ and ¼ in.; (3) determining the percentage by weight retained on each screen; and (4) recording the mechanical analysis in the following manner:

Passing ¾-in. screen .....	%
Passing ¾-in. screen and retained on a ¾-in. screen .....	%
Passing ½-in. screen and retained on a ½-in. screen .....	%
Passing 1-in. screen and retained on a 1-in. screen .....	%
.....	%
Total .....	100.00%

**For Sand or Other Fine Material with Broken Stone or Broken Slag.** The method shall consist of: (1) drying at not over 230° F. to a constant weight, a sample weighing in pounds 6 times the diameter in inches of the largest holes required; (2) separating the sample by the use of a screen having circular openings ¼ in. in diameter; (3) examining the portion retained on the screen in accordance with the method for broken stone or broken slag; (4) examining the portion passing the screen in accordance with the method for sand or other fine highway material; and (5) recording the mechanical analysis in the following manner:

Passing 200-mesh sieve .....	%
Passing 100-mesh sieve and retained on a 200-mesh sieve .....	%
Passing 80-mesh sieve and retained on a 100-mesh sieve .....	%
.....	%
Passing 10-mesh sieve and retained on a 20-mesh sieve .....	%
Passing ¾-in. screen and retained on a 10-mesh sieve .....	%
Passing ¾-in. screen and retained on a ¾-in. screen .....	%
Passing 1-in. screen and retained on a 1-in. screen .....	%
.....	%
Total .....	100.00%

**Elutriation Test for Sand or Fine Filler.** This test is adapted to fine mineral particles passing a 200-mesh sieve. Place 5 g. in a beaker about 120 mm. high, holding 600 cc., and fill almost to the top with distilled water at exactly 70° F. Agitate with compressed air until the mineral particles are brought into suspension, and in such a manner that no whirling results. Stop the blast and allow the liquid to stand exactly 20 seconds, whereupon the water above the sediment is immediately decanted through a 200-mesh sieve without, however, pouring off any of the sediment. The operations of agitation, sedimentation, and decantation are repeated with fresh water three times. The particles caught on the 200-mesh sieve are washed back into the sample remaining in the beaker, which is dried to constant weight and weighed. The difference represents the amount removed by elutriation, which should be expressed in percentage.<sup>1</sup>

**Specific Gravity.** Two methods are recommended, depending upon whether the particles are finer or coarser than 1 in. in diameter.

**For Aggregates Whose Particles are Less than ¼ In.** The Le Chatelier's flask is used for this purpose as described on p. 1199.

**For Aggregates Composed of Fragments Larger than ¼ In.** The Goldbeck apparatus<sup>2</sup>

<sup>1</sup> "Standard Forms for Specifications, Tests, Reports and Methods of Sampling for Road Materials," Bulletin No. 555, U. S. Dept. Agriculture, Wash., D. C., p. 32, Nov. 26, 1917.

<sup>2</sup> "Standard Forms for Specifications, Tests, Reports and Methods of Sampling for Road Materials," Bull. No. 555, U. S. Dept. of Agriculture, Wash., D. C., p. 31, Nov. 26, 1917.

illustrated in Fig. 164 is used for this purpose; 1000 g. of aggregate are dried to constant

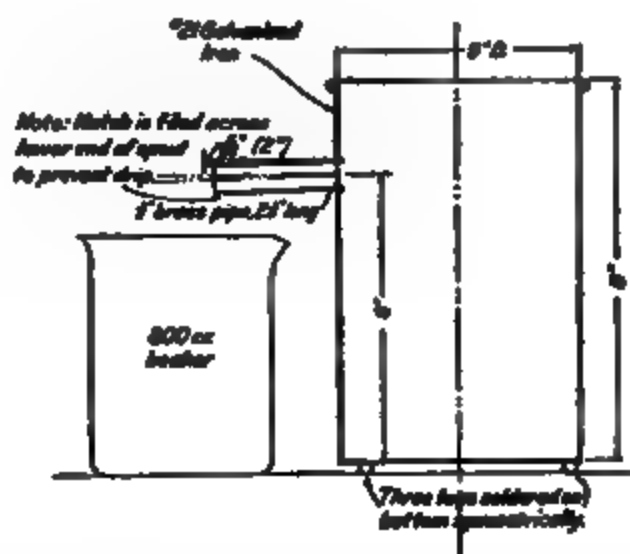


FIG. 164.—Goldbeck's Specific Gravity Apparatus.

weight, weighed to the nearest 0.5 g., and immersed in water for 24 hours. The pieces are then individually surface-dried with a towel, the sample reweighed and immediately introduced into the cylinder, which has previously been filled to overflowing with water at 77° F. The displaced water is caught in a tared beaker, and weighed. If the weight of the dry aggregate in air is  $a$ , and the weight of the displaced water  $b$ , then the apparent specific gravity is equal to  $a$  divided by  $b$ . The difference between the original weight of the specimen and its weight after 24 hours' immersion is used to determine the percentage of absorption. If  $c$  equals the weight of the water absorbed by the dry specimen in 24 hours, then the true specific gravity at 77° F. is equal to  $a$  divided by  $(b - c)$ .

**Chemical Analysis.** This may include a qualitative or a quantitative analysis, by any of the methods ordinarily used for this purpose. If a quantitative analysis is to be made, the reader is referred to other portions of this book, as well as to the following sources, viz.:

**Mineral Constituents Naturally Present and Added Fillers:** "Tentative Methods for Ultimate Chemical Analysis of Refractory Materials," Serial Designation: C 18-17 T), Proc. Am. Soc. Testing Materials, 17, Part I, 671, 1917; "Standard Specifications and Tests for Portland Cement" (Serial Designation: C 9-17), A. S. T. M. Standards, Adopted 1918, 506.

**Added White Pigments.** "Standard Methods for Routine Analysis of White Pigments" (Serial Designation: D 34-17), A. S. T. M. Standards, Adopted in 1918, 637.

**Added Yellow, Red or Brown Pigments.** "Standard Methods for Routine Analysis of Yellow, Orange, Red and Brown Pigments Containing Iron and Manganese" (Serial Designation: D 50-18), A. S. T. M. Standards, Adopted in 1918, 655.



## PART III

## EXAMINATION OF BITUMINIZED FABRICS

**This caption includes the following groups of products, viz.:**

- Q—Prepared roofings.
- R—Composition shingles.
- S—Deck and porch coverings.
- T—Bituminized fabrics for constructing built-up roofs.
- U—Bituminized fabrics for constructing waterproofing membranes.
- V—Electrical insulating tape.
- W—Waterproof papers for wrapping and packing.
- X—Waterproof papers for insulating against heat or cold.
- Y—Felt-base floor coverings (surfaced with linseed oil and pigment composition).
- Z—Expansion joints for pavements.

These are constructed as shown in Table IV, where the index  $a$  indicates that asphaltic compositions have been used, and  $t$  signifies that coal tar (pitch) et al., have been used.

TABLE IV.

[illegible]

## PHYSICAL TESTS OF FINISHED PRODUCT

**Weight.** Carefully unpack the fabric, and where any dusting finish has been used be sure not to detach it. Make certain that the specimen is of rectangular form, and then weigh it with an accuracy of at least 0.25%. Then measure its length and breadth with an accuracy of at least 0.25%, and figure its area. Calculate its weight per unit area from the following formulae:

$$\text{Lbs. per sq. ft.} = \frac{\text{gms.}}{\text{sq. cms.}} \times 2.5 = \frac{\text{gms.}}{\text{sq. ins.}} \times 0.317,$$

$$\text{Ozs. per sq. yd.} = \frac{\text{gms.}}{\text{sq. cms.}} \times 295 = \frac{\text{gms.}}{\text{sq. ins.}} \times 45.71.$$

**Pliability** is tested by cutting lengthwise from the center of the roll a strip 1 in. wide, and commencing with the largest, successively bending it around various cylinders under water at temperatures of 77 and 32° F., respectively, recording the cylinder on which the surface cracks. Five cylinders are used in the test, measuring 2½, 2, 1½, 1 and ½ cm. in diameter, respectively. A convenient apparatus for this purpose is shown in Fig. 165. The fabric should be bent parallel to itself, through an arc of 180°, at a uniform speed, and in exactly 2 seconds time.

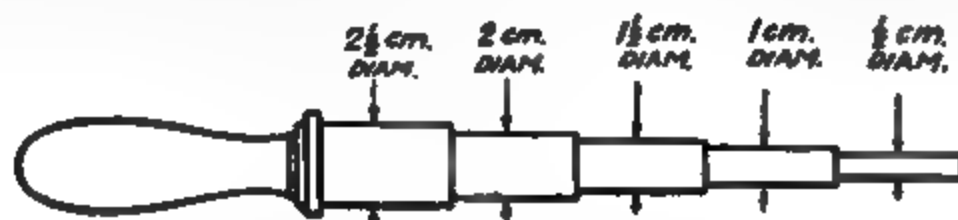


FIG. 165.—Mandrels for Testing the Pliability.

The pliability is expressed in figures from 1 to 10, as follows:

- 1 May be bent through an arc of 180° in one direction (i. e., flat on itself), and then through an arc of 360° in the other direction (i. e., flat on itself) without cracking the surface coatings.
- 2 May be bent flat on itself (i. e., through an arc of 180°) without cracking the surface coatings, but will crack when bent through an arc of 360° in the other direction.
- 3 Surface cracks when bent through an arc of 180° (flat on itself).
- 4 Surface cracks on the ½-cm. cylinder.
- 5 Surface cracks on the 1-cm. cylinder.
- 6 Surface cracks on the 1½-cm. cylinder.
- 7 Surface cracks on the 2-cm. cylinder.
- 8 Surface cracks on the 2½-cm. cylinder.
- 9 Both the surface and the interior of the sheet crack on the 2½-cm. cylinder without, however, cracking entirely through the sheet.
- 10 The sheet cracks entirely through on the 2½-cm. cylinder.

**Thickness**, in mils (thousandths of an inch) is determined with a micrometer caliper, having flat bearing surfaces about ¼ in. in diameter.

**Strength** is determined by subjecting a specimen cut in the direction of the length of the roll and of the dimensions shown in Fig. 166 to a tension which is increased at a uniform speed of 3 lbs. per second, the specimen being maintained at a uniform temperature of 77° F. during the test. A simple and effective instrument for finding the tensile strength is shown in Fig. 167. Ten such tests are averaged.

**Resistance to Heat.** A strip is cut exactly 12 in. × 12 in., care being taken not to disturb any of the detached mineral matter on the surface, and suspended in an oven from a thin wire fastened through holes in the upper edge of the strip. The piece should be allowed to hang freely and maintained at a temperature of 125° F. for 100 hrs. At the end of this time it is allowed to cool. The pliability, weight, thickness and strength are redetermined and the changes from the original figures expressed in percentages. Any change in the appearance of the surface should also be noted, e. g., sliding of the mineral matter, absorption of the coating by the fabric, any yellowing of the surface, blistering, etc.

**Resistance to Dampness.** Accurately cut a strip of the bituminized fabric 18 in.  $\times$  18 in., and weigh. Remove the detached mineral particles from both sides of the sheet with a moderately stiff brush, and reweigh (area equals  $2\frac{1}{4}$  sq. ft.). Suspend in a tight box containing sufficient water at the bottom to saturate the air with moisture. Cover tightly and allow the specimen to remain in the moist air for 100 hours at 77° F. As the moisture enters more readily through the cut edges of the sheet than through the surface itself, 6 in. should be trimmed from the edges at the termination of the test, leaving a strip measuring exactly 12 in.  $\times$  12 in., representing the central portion of the original specimen, and weighing  $\frac{4}{9}$  of the latter. Ascertain the weight, thickness and tensile strength of the 12  $\times$  12 portion at the end of the test, and calculate any variation in percentage from the original figures. The increase in weight should be figured on the basis of the original material including the detached mineral matter.



FIG. 166.—Tensile Strength Specimen.

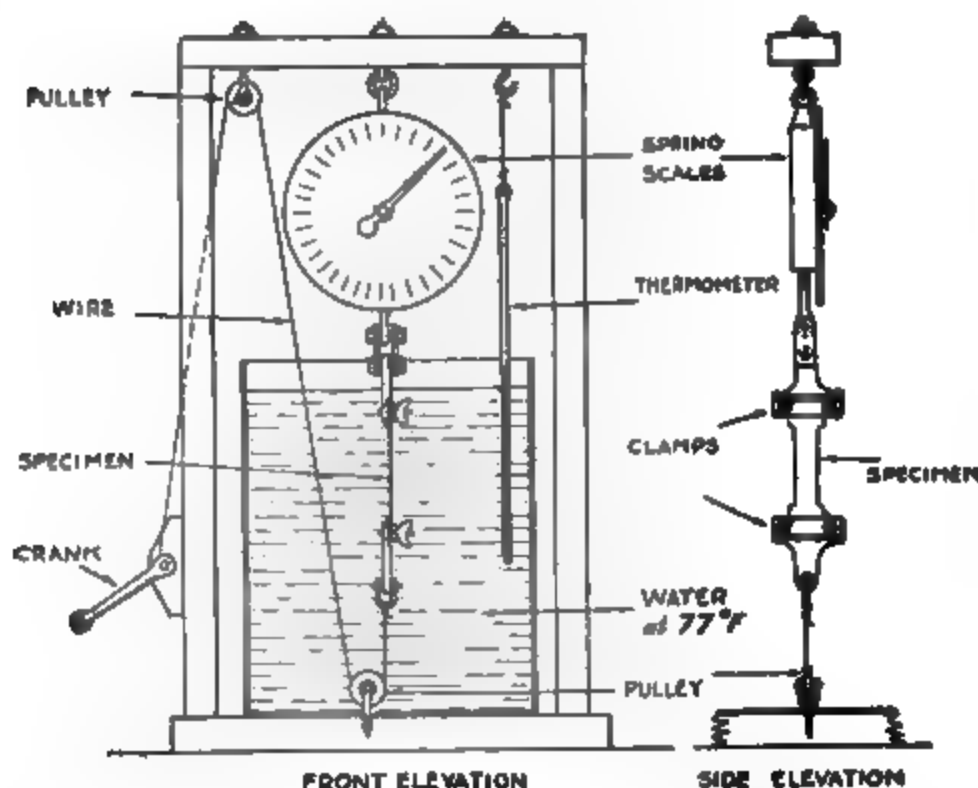


FIG. 167.—Instrument for Testing the Strength of Bituminized Fabrics.

**Resistance to Water.** This test is run exactly the same as the preceding, only in this case the specimen should be immersed entirely in water at 77° F. for 100 hours. An 18 in.  $\times$  18 in. sheet should be used in making the test, and trimmed to 12 in.  $\times$  12 in. before redetermining its weight, thickness or strength.

**Resistance to Electrical Current.** This test is applied to saturated and coated papers used for wrapping wires, cables and other insulative purposes, and consists in subjecting the paper at 77° F. to an alternating current of a frequency not over 65 cycles, the potential being increased at the rate of 125 volts per minute between flat disc terminals having bevelled edges, the areas of contact measuring exactly 1 sq. in. The terminals should be brought closely together, so that the paper will just slide between them, and the current increased until a breakdown occurs.

**Special Tests for Adhesive Insulating Tape.** (1) A strip protected from the direct rays of the sun, is hung indoors for 2 months. The diminution in tackiness is noted and is a measure of the extent to which it "dries out."

(2) The tensile strength is measured at 77° F. by separating a  $\frac{1}{4}$  in. specimen at the rate of 20 in. per minute, the initial distance between the jaws of the testing machine being 12 in.

(3) The adhesion of the compound between the plies is measured by winding a strip 2 ft. long and  $\frac{1}{4}$  in. wide upon a 1 in. mandrel under a tension of 7 $\frac{1}{2}$  lb. at the rate of 30 in. per minute, and then measuring the rate of separation per minute under a weight of 3 lb.

(4) A strip is first exposed to dry heat of 100° C. for 18 hours, cooled to room temperature, and then subjected to the test prescribed in (3), except that the weight applied to unwind the tape shall be 1 lb.

(5) The dielectric strength is recorded by winding the tape spirally with one third lap on a smooth copper rod, 1 in. in diameter, for a distance of 6 in. Two inches in the center are then covered with tin foil and bound down securely with tape, whereupon an alternating current of 1000 volts having a frequency of not over 65 cycles, is applied for 5 minutes between the metal rod and the tin foil, to observe whether a puncture occurs.

**Resistance to Weather.** For a detailed description of the procedure for conducting exposure tests on bituminized fabrics, and specifically composition roofings and shingles, the reader is referred to "Asphalts and Allied Substances" Second Edition published by D. Van Nostrand Co., New York, 1920, page 574 et seq.

## SEPARATION OF FINISHED PRODUCT INTO ITS COMPONENT PARTS

### Separation of Bituminous Matter, Mineral Matter and Fibrous Matter

#### SINGLE LAYERED FABRICS (SATURATED ONLY, OR COATED ONLY)

Moisture is determined by distilling a weighed quantity of the fabric, immersed in a bath of kerosene, in the apparatus illustrated under the heading "Water," Part I, and measuring the volume of water recovered in the distillate. From this, its weight is calculated in percentage based on the weight of fabric taken for analysis.

Treat another weighed specimen of the fabric, cut to a convenient size, in a Soxhlet extractor with carbon disulphide, and continue the extraction for several hours after the liquor syphons over colorless. Air-dry the extracted fabric, then heat it in a ventilated oven maintained at 110° C; cool in a desiccator, and weigh as rapidly as possible. Repeat the drying until the weight of the fabric remains constant, as determined by two consecutive weighings taken not less than 10 minutes apart, showing a further loss of not more than 0.1%. This gives its weight in the "bone-dry" state. The total weight of moisture present in the original material figured against the weight of "bone-dry" fabric, will give the percentage of moisture extant in the original fabric exclusive of the bituminous constituents.

Fabrics treated with asphalt become readily desaturated upon extracting with carbon disulphide, whereas fabrics treated with coal-tar or coal-tar-pitch will retain much of the "free carbon" mechanically. Most of the free carbon may be removed, however, by vigorously agitating the desaturated fabric with carbon disulphide in a stoppered flask. One or more such treatments will remove the bulk of the "free carbon," which in turn may be recovered upon filtering the washings.

The extracted fabric may be examined for ash, thickness and strength, also subjected to a microscopic examination to ascertain the fibres present, in accordance with the methods to be described.

Add any "free carbon," recovered as described above to the carbon disulphide extract, and evaporate the mixture, first on a steam bath, and then in an oven at 80° C., until the residue corresponds to the exact difference in weight between the original bituminized fabric and the combined weights of extracted "bone-dry" fabric plus the moisture present. The bituminous matter recovered in this manner may be examined as described later.

## 1340 EXAMINATION OF BITUMINOUS SUBSTANCES

### SINGLE LAYERED (SATURATED AND COATED) ALSO LAMINATED FABRICS

Since the fabrics and bituminous matter may be assembled in many different ways, the resultant products are too numerous to itemize. It is impractical, therefore, to give analytical methods applicable to each. The ones which follow have been devised specifically for examining prepared roofings and composition shingles.<sup>1</sup> These methods are typical ones, and with slight minor modifications and a little ingenuity, may be adapted to other forms of bituminized fabrics.

For all practical purposes, prepared roofings may be divided into the six types illustrated in Fig. 168.

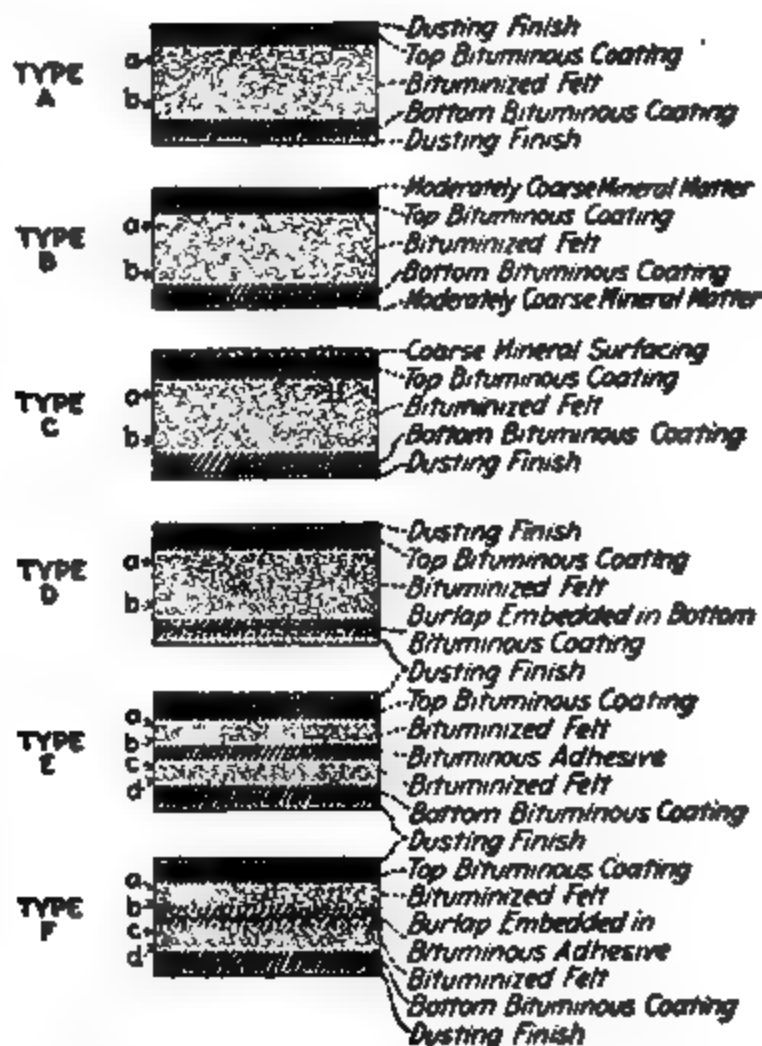


FIG. 168.—Types of Prepared Roofings.

Type A represents a layer of felt saturated and coated with bituminous matter. The surface coatings may be either finished plain or dusted with very fine mineral matter, and they may be either applied smooth and level or with a veined appearance.

Type B is similar to Type A, but surfaced on both sides with moderately coarse mineral matter embedded superficially in the coatings.

Type C is similar to Type A, but surfaced on one side with coarse mineral matter embedded in the coating.

Type D is composed of a layer of saturated felt and a layer of burlap or cotton duck cemented together and coated on top and bottom with bituminous matter. Its surface is finished similar to Type A.

Type E is composed of two layers of saturated felt cemented together and coated with bituminous matter, being finished on the surface similar to Type A.

Type F is composed of two layers of saturated felt, cemented together with a layer of burlap in between, and coated with bituminous matter. Its surface is finished as in Type A.

<sup>1</sup>"Analysis and Testing of Prepared Roofings," J. Ind. Eng. Chem., 9, 1048, 1917

## EXAMINATION OF BITUMINOUS SUBSTANCES 1341

The mineral matter, bituminous matter and fibrous matter are distributed in the following manner:

### MINERAL MATTER

- |   |   |   |
|---|---|---|
| 1—Detached.....   | } | <i>Very Fine Mineral Matter</i> (e.g., finely ground talc, mica or silica) Types A, D, E and F (on top and bottom) also Type C (on bottom only).      |
| 2—Embedded in the top surface coating                                 | } | <i>Moderately Coarse Mineral Matter</i> (e.g., sand, coarsely ground talc, and coarse mica flakes) Type B (on top and bottom).                        |
| 3—Embedded in the bottom surface coating                              | } | <i>Coarse Mineral Matter</i> (e.g., crushed slate, crushed brick or tile, crushed feldspar or granite, small pebbles or gravel) Type C (on top only). |
| 4—Admixed with the top surface coating (Types A, B, C, D, E and F)    | } | May or may not be present. If present, consists of very fine mineral matter (e.g., clay, silica, limestone, shale, colored mineral oxides, etc.).     |
| 5—Admixed with the bottom surface coating (Types A, B, C, D, E and F) | } |   |
| 6—Admixed with the cementing layer (Types E and F)                    | } |   |

### BITUMINOUS MATTER

- 1—Contained in the top surface coating (all types).
- 2—Contained in the bottom surface coating (all types).
- 3—Contained in the cementing layer (Types D and F).
- 4—Contained in the fabric, present in either one layer (Types A, B, C and D) or distributed in several layers (Types E and F).

### FIBROUS MATTER

- 1—One or more layers of felt (all types).
- 2—Burlap or other fabric (Types E and F).

The separation of prepared roofing into its component parts is carried out as follows:

*Weight Per 100 Sq. Ft.* Carefully unpack the roll, taking care not to detach any of the mineral surfacing or dusting finish. Weigh the roofing after removing the wrapper, ends, nails and lap-cement packed in the core of the roll. Measure the length and breadth of the roll with a steel tape, recording the dimensions to  $\frac{1}{8}$  in. Calculate the area in square feet.

Figure the weight of the finished roofing in lbs. per 100 sq. ft. .... (1)

Cut several strips *exactly* 3 in. wide *across* the sheet.

**NOTE**—With roofing 36 in. wide, these strips will measure exactly  $\frac{1}{3}$  sq. ft., and with roofing 32 in. wide, they will measure  $\frac{1}{4}$  sq. ft. Find the weight of each strip in grams.

Calculate the weight of the roofing in lbs. per 100 sq. ft. .... (2)

**NOTE**—With 36 in. roofing, wt. in lbs. per 100 sq. ft. =  $0.294 \times$  wt. 3 in. strip in grams.

With 32 in. roofing, wt. in lbs. per 100 sq. ft. =  $0.331 \times$  wt. 3 in. strip in grams.

**CHECK**—Result (1) should equal result (2).

*Detached Mineral Matter.* Remove the detached mineral particles from both sides of the 3-in. strips with a moderately stiff brush or cloth and reweigh in grams.

Calculate the weight detached mineral matter in lbs. per 100 sq. ft. .... (3)

*Dry Felt and Burlap; Total Embedded and Admixed Mineral Matter; Total Bituminous Matter.* Extract one of the 3-in. strips in a Soxhlet extractor with benzol. Dry the extracted fabric together with any adhering mineral matter at 110° C. Cool in a desiccator and weigh the felt as rapidly as possible before it has an opportunity to absorb moisture from the air. Repeat the drying, until the weight is constant. Carefully brush off, weigh and set aside the adhering mineral matter.

Calculate the weight of each layer dry felt or burlap in lbs. per 100 sq. ft. .... (4)

**NOTE**—Use the separated felt or burlap for examining its physical and chemical characteristics according to the methods to be described later.

Separate the mineral matter from the benzol extract by filtering or centrifuging; wash clean with successive portions of benzol, dry and weigh. Combine with the mineral matter brushed off the extracted felt.

Calculate the weight of the total embedded and admixed mineral matter in lbs. per 100 sq. ft. .... (5)

## 1342 EXAMINATION OF BITUMINOUS SUBSTANCES

Screen through a set of standard sieves of different mesh. A mere inspection of the particles retained by the various screens will enable one to distinguish the moderately coarse or coarse embedded mineral matter from any very fine admixed mineral matter present in Types B and C.

Calculate the weight of moderately coarse or coarse embedded mineral matter in lbs. per 100 sq. ft. for Types B and C; or calculate the combined weight of very fine embedded mineral matter and admixed mineral matter in lbs. per 100 sq. ft. for Types A, D, E and F

Calculate the total weight of bituminous matter in lbs. per 100 sq. ft., i.e. [1] - [(3) + (4) + (5)]

*Bituminous Saturation in the Felt.* Warm a strip about 2 in. wide cut lengthwise from the roll, and tear off the coatings as shown in Fig. 169, taking care that in so doing

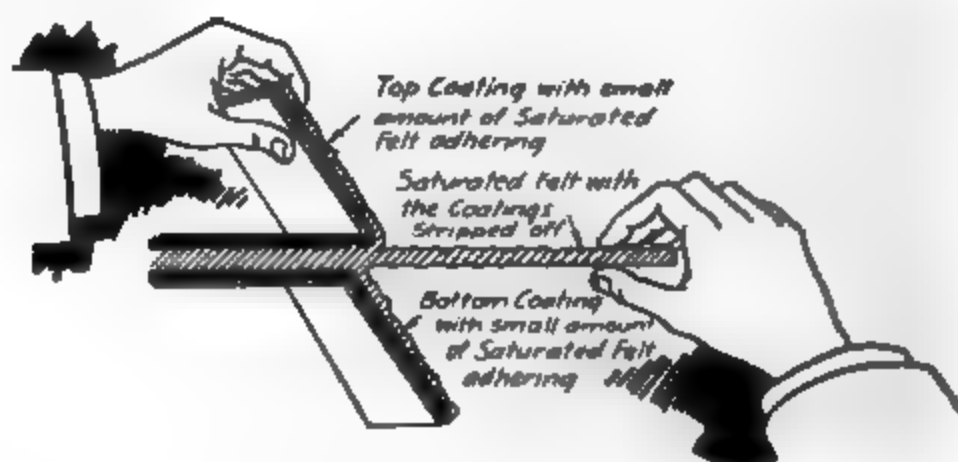


FIG. 169.—Method of Stripping the Coatings from the Saturated Felt.

as little as possible of the saturated felt is removed with the coatings, and, on the other hand, that none of the coatings or cementing layer remain adhering to the strip of saturated felt. The small arrows to the left of the various types of roofing illustrated in Fig. 168 indicate approximately where the layers should be separated. This can readily be accomplished with a little practice and dexterity. Where the roofing is composed of one layer of felt, as in Types A, B, C and D, the zone between the arrows *a* and *b* should be separated. Where the roofing is composed of two layers of felt, as in Types E and F, separate the zones between the arrows *a* and *b*, also *c* and *d*, respectively. In this manner, about 25 g. of the saturated felt (free from the coating or cementing layers) are obtained from each layer. Weigh and extract each portion separately in a Soxhlet with benzol. Dry the extracted felt at 110° C. to constant weight, desiccate and weigh. Calculate the weight of bituminous saturation by difference, and evaporate the benzol extract to exactly this weight.

**Note**—Use the residue of bituminous saturation recovered from each layer of felt for examining its physical and chemical characteristics, according to the methods described later

Calculate the per cent of bituminous saturation carried by each layer of dry felt. (8)

Calculate the weight of bituminous saturation present in each layer of the felt in lbs. per 100 sq. ft. [i.e. (8) × (4)]

*Weights of Bituminous Matter in the Coatings and Cementing Layer.*—In types A, B, C and D. The combined weights of bituminous matter in the top and bottom coatings in lbs. per 100 sq. ft. may be calculated by subtracting (9) from (7). To find the respective weights of bituminous matter in the top and bottom surface coatings, take a 3-in. strip cut across the sheet of roofing, from which the detached mineral matter has been removed, and split it lengthwise by tearing the felt midway between the points *a* and *b* (Fig. 168). Weigh and extract each section separately in a Soxhlet. Desiccate and weigh the dry felt in each section (and the burlap in Type D), also separate and weigh the total embedded and admixed mineral matter. Calculate the weight of bituminous saturation present [i.e., weight of dry felt × (8)]. From the original weight of each section subtract the combined weights of dry felt, bituminous saturation, embedded and admixed mineral matter. The difference represents the weight of bituminous matter in the surface coating carried by that particular section.

Calculate the weights of bituminous matter in the top and bottom coats, respectively, in lbs. per 100 sq. ft.

(10)

In Types E and F. Take a 3-in. strip freed from the detached mineral matter as previously described, and split it into three sections, by tearing through the felt midway between the points *a* and *b*, also *c* and *d*, respectively (Fig. 168). Weigh and extract each of the three sections separately in a Soxhlet. Separate, and in each case weigh the dry felt (also the burlap in Type F) and the total mineral matter. Following the method previously described:

- Calculate weights of bituminous matter in the top and bottom coats respectively in lbs. per 100 sq. ft. . . . . (11)  
 Calculate weight of bituminous matter in the cementing layer in lbs. per 100 sq. ft.  
 Calculate weight of very fine mineral matter admixed with the cementing layer in lbs. per 100 sq. ft.

*Very Fine Embedded Mineral Matter also Admixed Mineral Matter, in the Top and Bottom Coatings Respectively.* In types A, D, E and F. Take another 3-in. strip from which the detached mineral matter has been brushed off, and remove the outer layer of the top and bottom coatings respectively, by means of moderately rough sand paper. Enough of the surface should be scraped to remove every vestige of the very fine embedded mineral matter, and at the same time care should be taken not to cut completely through the surface coatings into the saturated felt underneath.

In types A and D, split the scraped sheets lengthwise midway between the points *a* and *b*. In types E and F, split the scraped sheets lengthwise midway respectively, between the points *a* and *b*, also *c* and *d*, discarding the central section. Extract the scraped outer sections separately with benzol as before, recovering and weighing:

- The dry felt present in the respective scraped sections . . . . . (12)  
 The admixed mineral matter present in the scraped sections. . . . . (13)  
 The total bituminous matter present in the surface coating and saturating the felt in the respective scraped sections. . . . . (14)

The dry burlap (in Type D).  
 Calculate the bituminous matter present in the felt in the respective scraped sections  $[(8) + 100 \times (12)]$ . . . . . (15)

Hence the bituminous matter present in the surface coating remaining on the respective scraped sections =  $(14) - (15)$ . . . . . (16)

The proportion of very fine mineral matter admixed with the bituminous matter in each coating =  $(13) + (16)$  . . . . . (17)

Total weight of very fine mineral matter admixed with the respective coatings in lbs. per 100 sq. ft. =  $(17) \times (10)$  [in Types A and D] or  $(17) \times (11)$  [in Types E and F]. . . . . (18)

And weight of very fine mineral matter embedded in the surface of the respective coatings in lbs. per 100 sq. ft. =  $(6) - (18)$ .

*Nature of the Bituminous Matter in the Coatings and Cementing Layer.* Brush off the detached mineral matter from a surface about 2 sq. ft. in area. Then scrape off the outer portion of the surface coating with a sharp knife. This is accomplished by holding the knife at right angles to the sheet of roofing resting on a firm, level surface, and rapidly drawing the blade sideways under moderate pressure. Care should be taken to avoid scraping entirely through the surface coating. This is important. Weigh and then dissolve the scrapings in benzol. Separate the mineral matter by filtering or centrifuging, and wash with successive portions of benzol. Dry and weigh the mineral matter. Calculate the weight of bituminous matter in the scrapings by difference, and evaporate the combined benzol extracts on the water bath to exactly this weight, completing the evaporation if necessary in an oven. Both surface coatings should be treated separately in this manner. In Type D the bottom coating may readily be removed by cooling the specimen in an ice-chest and rapidly tearing off the burlap, which will carry most of the bottom coat with it. This should be extracted, filtered and the extract evaporated to obtain the pure bituminous matter present.

In type F the central web of burlap may be torn out, and the bituminous matter contained in the cementing layer separated in the same manner.

In type E the bituminous matter may be separated from the cementing layer between the sheets of felt, by cooling in an ice-chest, rapidly tearing the specimen in two along the plane of the cementing layer, scraping and separating the bituminous matter as described for the surface coatings.

Use the separated bituminous matter for examining its physical and chemical characteristics.



## Examination of Separated Fabric

**Weight.** This is ascertained as described under "Physical Tests of Finished Product." It is expressed arbitrarily by the trade in terms of the "number" as follows:

- (a) In the case of paper, the "number" usually corresponds to the weight in pounds of a ream, consisting either of 500 sheets, for light papers, or 480 sheets, for heavy papers, each sheet measuring 24 in. by 36 in. Other arbitrary methods are also sometimes used embodying a different number of sheets, or sheets of other sizes. The following formulae will be found useful in calculating the "number":

$$\text{"Number"} (500: 24 \times 36) = \frac{\text{gms.}}{\text{sq. cms.}} \times 6150 = \frac{\text{gms.}}{\text{sq. ins.}} \times 953,$$

$$\text{"Number"} (480: 24 \times 36) = \frac{\text{gms.}}{\text{sq. cms.}} \times 5903 = \frac{\text{gms.}}{\text{sq. ins.}} \times 914.$$

In stating the "number," the percentage of moisture present in the paper should also be given.

- (b) In the case of felt, the "number" represents the weight in pounds of a ream consisting of 480 sheets, each measuring 12 in.  $\times$  12 in., the moisture content of which is arbitrarily set at 3.5%. The following formula may be used:

$$\text{"Number"} (480: 12 \times 12) = \frac{\text{gms.}}{\text{sq. cms.}} \times 983 = \frac{\text{gms.}}{\text{sq. ins.}} \times 152.$$

- (c) In the case of textile fabrics, the "number" represents the weight in ounces per lineal yard of a specified width, the moisture content being arbitrarily fixed at 6.5%. With burlaps the width is 40 in., with "regular" ducks 29 in., etc.

**Thickness.** This is found as described under the heading "Physical Tests of Finished Product."

**Strength.** The strength is determined by one of the following methods:

- (a) In the case of paper, the desiccated material is exposed for at least 2 hours in an atmosphere of 65% relative humidity, at 70° F.,<sup>1</sup> and while in this condition it is tested by means of a Mullen tester, increasing the tension at a uniform speed of 2 lb. per second until the specimen ruptures.
- (b) In the case of felt, expose the desaturated fabric for 3 days to air at 77° F., completely saturated with moisture, and then find its tensile strength as in (a). The reason for this is because the strength of the dry felt is increased materially during the process of extracting with solvents, but it may again be brought to correspond closely with its original strength by treating as described.
- (c) In the case of textile materials (e.g., cotton cloth, duck, burlap, etc.), it is customary to find the tensile strength when the desiccated fabric has assumed a moisture regain, established arbitrarily at 6.5% of its bone-dry weight.<sup>2</sup> Two methods are used for finding the tensile strength. One is known as the "Strip Test," in which a strip of the fabric, measuring 7 in. by 1½ in., ravelled to exactly 1 in. width, is clamped at each end by the jaws of the testing machine (measuring 1½ in.  $\times$  1½ in.), and strained to the point of rupture. The initial distance between the jaws is 3 in. and their speed of separation 20 in. per minute. The other method is known as the "Grab Test," in which the machine jaws, each of a definite area (i.e., 2 in. by 1 in.) are made to reach into the body of a rectangular piece of fabric 5 in. by 2 in., and clamped exactly 1 in. apart. The jaws are separated at a speed of 12 in. per minute to the point of rupture. In each method 5 tests are averaged separately for the warp and filling.

**Thickness Factor.** This is equal to the thickness in mils divided by the "number" of the fabric.

**Strength Factor.** This is equal to the strength in pounds divided by the "number" of the fabric.

**Ash.** The ash is determined by incineration and calculated in percentage.

<sup>1</sup> Mittheilungen a.d.K. Technischen Versuchungsanstalten, 7 (1889), 2; 8 (1890) 8 to 19; "A Constant Temperature and Humidity Room for the Testing of Paper, Textiles, etc.," by F. P. Veitch and E. O. Reed, J. Ind. Eng. Chem., 10, 1918, 38.

<sup>2</sup> "Tentative General Methods for Testing Cotton Fabrics" (Serial Designation: D 39-18 T.), Proc. Amer. Soc. Testing Materials, Part I, Appendix V, 18, 709, 1918; also "Effect of Moisture on the Tensile Strength of Aircraft Fabrics," by G. H. Haven, *ibid.*, page 380.

**Fibres Present.** The percentage composition of the fibres is determined microscopically by staining them with a solution of zinc-chlor-iodide (prepared by dissolving 4 g. of potassium iodide and 0.1 g. of iodine in 12 cc. of water, and then adding 20 g. of zinc chloride), and counting under a microscope having a magnification of about 100 diameters. The individual fibres are recognized by their characteristic shapes and the colors they are stained by the zinc-chlor-iodide solution. The percentages are ascertained by counting the fibres in a number of fields and finding their average. The following classes of fibres are reported:

Rag Fibres	Cotton fibres—stained wine-red
	Wool fibres—unstained by the solution
	Jute and manila fibres—stained a yellowish brown
Paper Fibres	Mechanical wood pulp—stained lemon-yellow
	Chemical wood pulp (sulphite and soda)—stained grayish purple to purple

The following solution has been suggested for distinguishing the different kinds of chemical wood pulp, including unbleached and bleached sulphite pulps.<sup>1</sup> The fibres are first moistened with a 5 per cent solution of ammonium molybdate and then with a solution of paranitroaniline (200 mg. dissolved in 80 cc. of distilled water, to which are added 20 mg. sulphuric acid, sp.gr. 1.767). This stains the fibres as follows:

Mechanical wood pulp	..... bright reddish orange
Unbleached sulphite pulp	..... faint dull orange to faint brownish
Bleached sulphite pulp and soda pulp	..... colorless.

Another reagent recently proposed for this purpose<sup>2</sup> is prepared by mixing equal volumes of N/10 ferric chloride and N/10 potassium ferricyanide solutions. The moist fibres are immersed for 15 minutes at a temperature of 35° C., removed and washed thoroughly with water. They are then immersed in a freshly prepared red stain composed of: benzopurpurin 4-B extra (Bayer & Co.) 0.4 g.; oxamine brilliant red BX (Badische Co.) 0.1 g.; and distilled water 100 cc. This is maintained at 45° C. for 5–6 minutes, the fibres thereupon removed, washed immediately with water, and examined under a microscope. Unbleached sulphite pulp, ground wood, jute, or any lignified fibres are stained a deep blue (the depth depending upon the lignin content); whereas bleached sulphite pulp, soda pulp, rags, wool or any thoroughly bleached fibres are stained a brilliant red.

Manila fibres may be differentiated from other rope fibres (*e.g.*, sisal, New Zealand, istle, Mauritius and maguey)<sup>3</sup> by immersion for 20 seconds in a solution of chloride of lime (containing about 5% of available chlorine) freshly acidulated with acetic acid (2 cc. of glacial acetic acid per 30 cc. chloride of lime solution); rinsing with water; then rinsing with 95% alcohol; and finally suspending the fibres over strong ammonia for 1 to 2 minutes. In 3 to 4 minutes thereafter, Manila fibres will turn brown, whereas the other rope fibres mentioned will assume a cherry red color.

### Examination of Separated Bituminous Coatings, Saturating and Cementing Compounds

The bituminous compounds separated in their pure state as described above should be tested as outlined in Part I.

### Examination of Separated Mineral Surfacing and Admixed Mineral Matter

The mineral ingredients separated in their pure state as described are examined as outlined in Part II, "Examination of Separated Mineral Matter."

<sup>1</sup> "Paper Reagent," by W. J. Schepp, Chemist Analyst, p. 20, September, 1917.

<sup>2</sup> "A Method to Distinguish between Bleached and Unbleached Sulphite Pulps," by C. G. Bright, J. Ind. Eng. Chem., 9, 1044, 1917.

<sup>3</sup> "Distinguishing Manila from All Other Hard Rope Fibres," by C. E. Swett, J. Ind. Eng. Chem., 10, 227, 1918.

## PART IV

EXAMINATION OF BITUMINOUS-SOLVENT COMPOSITIONS  
(I.E., CEMENTS, PAINTS, VARNISHES, ETC.)

Bituminous paints, cements, varnishes, enamels and japans are all characterized by the presence of a volatile solvent with a bituminous base, combined in the form of "vehicle." Depending upon whether or not the bituminous paints and cements contain a pigment or filler, they may be divided into two general classes, viz.:

(1) Pigment or filler absent: including bituminous varnishes and japans also certain bituminous paints and cements.

(2) Pigment or filler present: including bituminous enamels, also certain bituminous paints and cements.

The first class consists of a vehicle made up of a solvent and base. The second consists of a pigment or filler combined with a vehicle, the latter similarly being made up of a solvent and base. The bituminous base may be composed of bituminous matter, with or without the presence of animal and vegetable oils or fats, resins or metallic dryers. In making an analysis of the paint, cement, varnish, enamel or japan, the following components are separated and examined viz.: (1) solvent, (2) pigment or filler, (3) base.

## PHYSICAL TESTS OF FINISHED PRODUCT

**Specific Gravity.** This may be ascertained by any of the methods described in Part I, care being taken to prevent evaporation of the solvent. The weight per gallon may be calculated from the specific gravity, by multiplying by 100 and dividing the product by 12.

**Viscosity.** The Engler Method may be used if the composition is sufficiently liquid, otherwise special instruments must be employed for the purpose.

**Spreading Capacity.** The paint or varnish should be spread on a clean metal surface by skilled workmen under actual working conditions, and the factors of light, temperature and moisture carefully noted. The area covered by one gallon under the conditions noted is an index of its spreading capacity.

**Drying Properties.** The time which elapses when the coating ceases to be tacky in the preceding test is an indication of the rate with which the composition dries.

**Covering Power.** A portion of the material is spread on a glass plate at the same rate as noted in the spreading capacity test, and when dry the opacity is recorded under conditions which may be duplicated readily.

**Exposure Test.** The composition is applied to the surface for which it is intended under carefully controlled working conditions and exposed to the direct action of the weather. The appearance of the surface is noted and recorded at periodic intervals until the coating no longer fulfils its protective action.

## SEPARATION OF FINISHED PRODUCT INTO ITS COMPONENT PARTS

**Solvent.** *Rapid method used for determining the percentage of solvent present:*

The method devised by A. L. Brown is rapid and gives accurate results, but does not recover the solvent for further examination.<sup>1</sup> Deliver 3-4 cc. of the well-mixed material (cements as well as paints of a heavy body should first be thinned to fluid consistency with a weighed quantity of pure benzol) from a 10-cc. pipette into a weighed glass flask of 50 cc. capacity, as rapidly as possible. Stopper the flask immediately, weigh, and dilute to the mark with pure benzol. Deliver exactly 10 cc. of the well-mixed material from the pipette upon a weighed ground-glass plate, 10 by 15 cm. and 1.5-3.0 mm. thick, supported in a level position. The diluted material should be

<sup>1</sup> "Quantitative Determination of Body and Solvent in Varnish," by A. L. Brown, Proc. Am. Soc. Testing Materials, 14, Part II, 467, 1914; "Determination of Volatile Thinner in Oil Varnish," by E. W. Boughton, Technologic Paper No. 76, Bureau of Standards, Wash. D. C., June 21, 1916.

flowed gradually on the plate, the object being to cover it entirely, without causing the solution to creep over the edges. It is recommended that 7 cc. be delivered first, and the remainder, a few drops at a time during the ensuing 2 minutes. The evaporation of the benzol will carry most of the solvent with it, and the film is so thin that the solvent will evaporate in 1½–2½ hours, the plate being weighed every half hour to follow the course of evaporation. Should the material contain a drying oil, the plate must be placed in an atmosphere of illuminating gas after the first half hour, replacing it after each weighing. The solvent has entirely evaporated when a constant weight is obtained. From this calculate the percentage of solvent by weight. An idea of the drying qualities of the film may be gained by placing the glass in a free circulation of air after the solvent is eliminated, and weighing it every hour as the film oxidizes, until it no longer increases in weight. If the coating has a tendency to dry unevenly, a weighed quantity of 50-mesh sea sand, previously dried and ignited, may be sifted over the paint in a very thin layer, but so the paint will be visible between the grains of sand. This will insure a uniform evaporation of the solvent.

*Method Used for Recovering the Solvent for Its Examination and Identification.* Distil 100 g. paint in a 500-cc. flask, connected with a spray-trap and a vertical condenser and pass through it a current of dry steam, the flask being heated in an oil bath to 100° C. As the steam passes through, gradually raise the temperature of the bath to 120° C. Catch the distillate in a separatory funnel, continuing the distillation until the funnel contains 400 cc. of water. To prevent frothing and bumping, it is advantageous to weigh a small piece of broken glass or pumice-stone into the flask. Let the distillate stand until it separates into two layers, then draw off the water and determine the volume and weight of solvent recovered. Weigh out another 100 g. into a 250-cc. flask and distil without steam over an electric stove. Continue the distillation until the residue in the flask reaches a temperature of 200° C. This gives somewhat lower results than the first method, but the distillate should be tested for water soluble substances to correct the results obtained by the previous method. Turpentine dissolves to the extent of 0.3 g. for each 100 cc. of water condensed.<sup>1</sup>

*Pigment and Filler.* Dilute 100 g. of the well-mixed material with 500 cc. of benzol in an 800-cc. stoppered flask. Either centrifugate or let stand in a warm place until the pigment or filler has settled, then carefully decant the supernatant liquid into a clean flask of large capacity. The pigment or filler is shaken up with 250 cc. more benzol, allowed to stand in a warm place until it settles, and the supernatant liquid decanted into the second flask. Repeat the treatment with benzol until the vehicle has been completely extracted from the pigment. The combined extracts are allowed to stand quietly to recover any pigment that may have been carried over with the benzol, and then carefully decanted through a weighed Gooch crucible provided with an asbestos filter. The residues in the flask and on the Gooch crucible are washed with benzol as before, and combined with the balance of pigment or filler which is then dried at 110° C. and weighed. The pigment or filler thus extracted is used for a qualitative or quantitative analysis.<sup>2</sup>

*Base.* The combined extracts of the preceding test are distilled to a small bulk, transferred to a tared dish, and evaporated in an oven at 110° C. exactly to the calculated weight of the base, by subtracting the weights of solvent and pigment or filler from the original weight of material taken for examination. When oxidizable substances are present, the final evaporation should take place in an atmosphere of illuminating gas.

The base recovered in this manner will contain the bituminous material (with the exception of the "free carbon" which will be separated with the pigments), animal and vegetable oils or fats, resins and metallic bases and dryers. It should be tested by the methods described in Part I, to identify the materials used in its manufacture, or to aid in its duplication. It may be separated into its component parts as follows:

<sup>1</sup> "Some Technical Methods of Testing Miscellaneous Supplies," by P. H. Walker, Bulletin No. 100, Revised, Bureau of Chem., U. S. Dept. of Agri., Wash., D. C., Feb. 20, 1910.

<sup>2</sup> "Analysis of Paints and Painting Materials," by H. A. Gardner and J. A. Schaeffer, N. Y., 1911.

# 1348 EXAMINATION OF BITUMINOUS SUBSTANCES

## Method of Analyzing the Separated Base

Dissolve 50 g. in 150 cc. benzol. Add 10 cc. dil. nitric acid (1 : 1) and boil under a reflux condenser for  $\frac{1}{2}$  hour to decompose any metallic soaps (i.e., driers, etc.). Add 150 cc. water, boil under reflux condenser, transfer to a separatory funnel, draw off the aqueous layer, boil with another 100 cc. water, and repeat if necessary until all the metals are removed.

<b>Benzol Solution:</b> Distil to 100 cc., add 300 cc. of the saponifying liquid, boil under reflux condenser for 1 hour, and separate the unsaponifiable and saponifiable constituents as described.			<b>Aqueous Extract:</b> Contains the metallic bases as nitrates. Examine qualitatively and then quantitatively for lead, manganese, cobalt, zinc, calcium, and magnesium. (N.B.—The last three used for hardening rosin. The metallic driers should not be found by ignition, since the lead will be reduced to metal by the organic matter, and volatilized.)
<b>Unsaponifiable Matter:</b> If higher alcohols are present they may be extracted by boiling with twice the weight of acetic anhydride and filtering:	<b>Saponifiable Matter:</b> Separate the fatty and resin acids as described on p. 1175.	<b>Aqueous Layer:</b> Determine percentage glycerol. Multiply this by 10 to estimate percent of vegetable or animal oils or fats (triglycerides) present in the original substance. (Note "C").	
<b>Hydrocarbons: Higher Alcohols Etc.:</b> Contain the bituminous substances (i.e., asphalt, coal-tar, pitch, unsap. matter derived from fatty-acid pitch, etc.). Examine by the methods included in Part I.	<b>Fatty Acids: Resin Acids:</b> Include acids derived from vegetable and animal oils or resins, also from fatty-acid pitch. (Note "A").		
<b>Higher Alcohols Etc.:</b> Contain cholesterol, etc. derived from wool grease, also the unsaponifiable constituents originally present in resins (4 to 8%). (See p. 1134.)			

## Note "A"

The following means are used to distinguish between the fatty acids derived from oxidized vegetable or animal oils and fatty-acid pitch respectively:

	Fatty Acids Derived From Vegetable or Animal Oils	Fatty Acids Derived From Fatty-acid Pitch
Lactone Value	Less than 25	Greater than 25
K. and S. Fusing-point	Less than 80° F.	Greater than 80° F.
Hardness at 77° F.	Less than 5.0	Greater than 5.0
Color in Mass	Translucent yellow to brown	Opaque brown to black

## Note "B"

Test qualitatively for rosin by the Liebermann-Storch reaction (p. 1139). Fossil resins may be distinguished from rosin by determining the saponification, acid anhydride, and ester values of the mixed resin acids. The following figures have been reported on the resin acids separated as described:<sup>1</sup>

<sup>1</sup> "The Determination of Rosin in Varnishes," by A. H. Gill, J. Am. Chem. Soc. 28, 1723, 1906; "Shellac Analysis," by E. F. Hicks, 8th Intern. Cong. of Applied Chem. 12, 115, 1912.

	Saponification Value	Acid Value	Ester Value
Straight Rosin Varnish . . . . .	182-185	160-162	22-24
Rosin $\frac{1}{2}$ ; Kauri $\frac{1}{2}$ Varnish . . . . .	122-135	44-62	72-78
Rosin $\frac{1}{4}$ ; Kauri $\frac{3}{4}$ Varnish . . . . .	143.5	88	55.5
Straight Kauri Varnish . . . . .	130	45	85
Untreated Rosin . . . . .	165-180	155-170	0-13
Untreated Kauri Gum . . . . .	124	41	83

Other resins may be examined in a like manner, although unfortunately, figures are not at present available.

*Note "C"*

If this corresponds with the total saponifiable matter present, then fatty-acid pitch and resins are absent.

## PART V

### EXAMINATION OF BITUMINOUS EMULSIONS

These include bituminous emulsifying oils used for laying dust "dust palliatives," also bituminous emulsions used for waterproofing Portland-cement mortar and concrete. The following products are likely to be present, viz.: water, ammonia, various chemicals, bituminous matter, animal and vegetable oils or fats, other forms of non-bituminous organic matter and mineral matter.

Water is determined as described. Ammonia is liberated by rendering alkali with caustic potash and heating. If present, it is detected by its odor, and may be determined quantitatively by distilling into a standard solution of sulphuric acid and retitrating with alkali. The presence of chemicals may be detected by boiling with water, acidifying with hydrochloric acid and extracting the bituminous and fatty substances with benzol. The chemicals remain in the aqueous layer and may be determined by a qualitative or quantitative analysis. Bituminous matter is determined by saponifying the material and then extracting the unsaponifiable constituents as described. The non-bituminous organic matter and the chemicals are separated from the bituminous and fatty matters as previously described, and the non-bituminous organic matter in turn separated from the chemicals by suitable methods. Mineral matter is determined by incinerating a weighed quantity of the material and examining the ash as described.

### Method of Proximate Valuation of Oil Shale

The following is the outline of the method used in the Colorado School of Mines.<sup>1</sup>

Two hundred and forty-one grams of shale (219.1 g. in case of rich ore) are placed in an iron retort (*A*, Fig. 169a), 20 cc.  $\text{N.H}_4\text{SO}_4$  are placed in the tube (*F*) and the apparatus connected up as shown. After testing for leaks the shale is gradually heated, beginning with a low heat and increasing to the full heat of three Scintaco burners. The heating is continued until no more gas is evolved (3-5 hrs.). The oil is caught in the cylinder (*B*), the ammonia is caught in the acid of the tube (*F*) and determined as stated below. The gas is measured by the water displacement in the carboy (*I*).

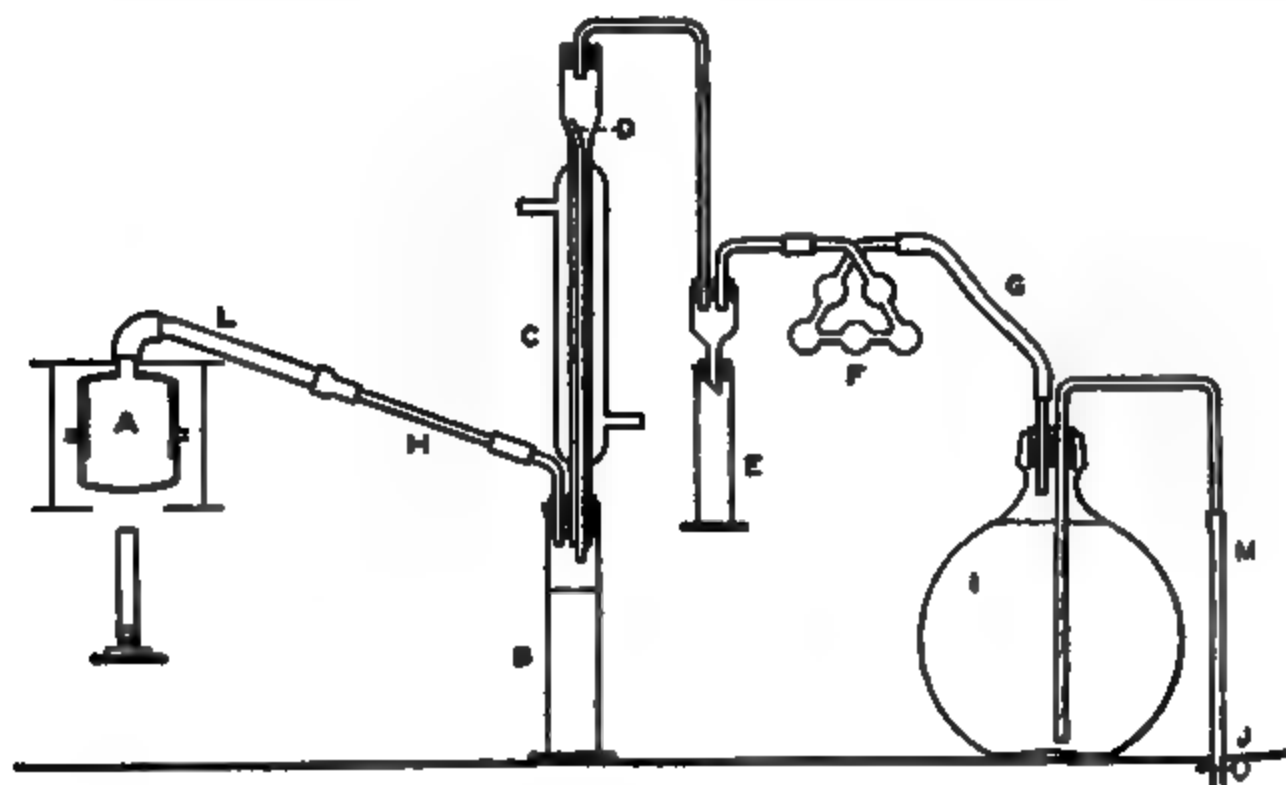


FIG. 169a.

If 241 g. sample is taken

cc. oil obtained  $\approx$  gallons per ton of shale,

cc. gas  $\times 0.1337 \approx$  cubic feet gas per ton of shale,

Grams spent shale in retort  $\times 8.3 \approx$  lbs. shale per ton.

**Ammonia as Sulphate.** The acid in (*E*) and the rinsings of (*C*), (*D*) and (*E*) are placed in a flask.  $\text{CO}_2$  is expelled by boiling. The free acid is just neutralized with  $\text{NaOH}$  (litmus or cochineal ind.), 10 cc. neutral 40 per cent. formaldehyde added and the solution boiled 1 minute. The liberated  $\text{H}_2\text{SO}_4$  is now titrated with  $\text{N}/5 \text{ NaOH}$ .



1 cc.  $\text{N}/5 \text{ NaOH} \approx 0.10954 \text{ lb. } (\text{NH}_4)_2\text{SO}_4 \text{ per ton shale.}$

<sup>1</sup> The Oil Shale Industry, by Victor C. Alderson, President of C. S. M., Golden, Colo.

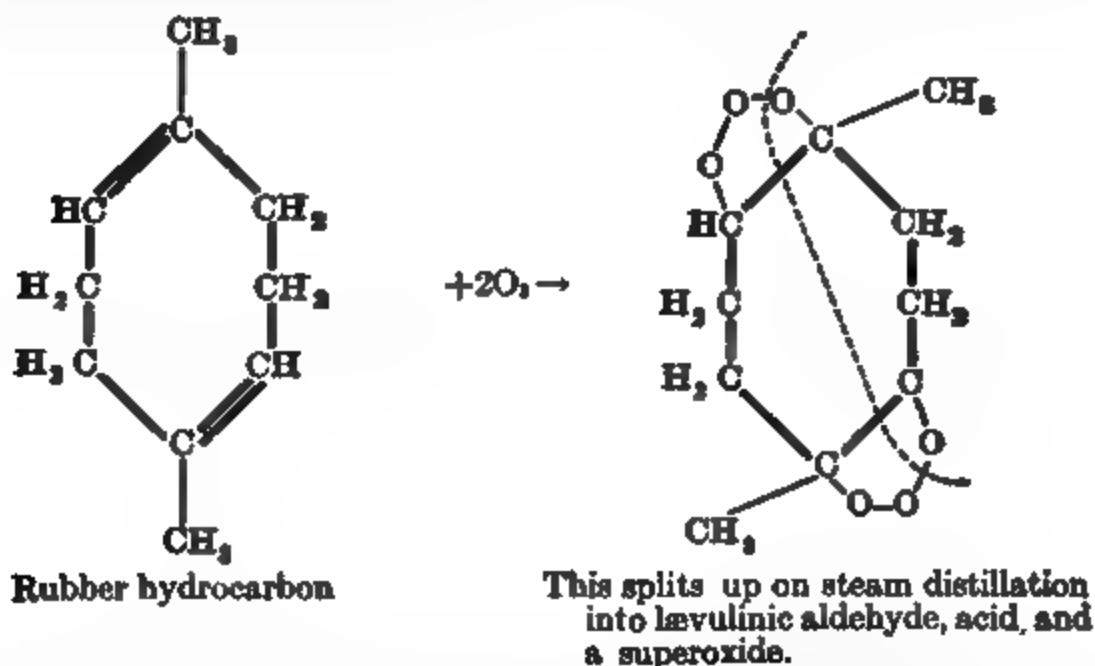
# RUBBER

By L. E. SALAS, M.A., B.Sc.

**Rubber** is obtained from the latex of certain plants belonging to the Natural Orders, *Euphorbiaceae*, *Apocynaceae*, *Urticaceae*. The latex is a "milky" juice showing Brownian movement; an emulsoid of rubber in a watery serum, and it is associated with many other substances (resins, sugars, protein). The chief rubber-bearing plants are *Hevea brasiliensis* (Pará), *Castilloa*, *Ficus* and the *Landolphia*s. In *Parthenium argenteum* (Guayule) the rubber occurs solid in the parenchyma.

The **function** of the rubber in the plant is unknown. The resins are considered as degradation products. The protein acts as a protective colloid preventing the coalescence of the globules in the latex, and coagulation consists in destroying this protection. Coagulation is brought about by heat, or chemical reagents, or both.

The **essential constituent** of rubber is a hydrocarbon (caoutchouc). It is a poly-prene, or polymerized terpene,  $(C_{10}H_{16})_n$ . The physical differences of the various rubbers are due to variation in chemical aggregation or the value of  $n$ , i.e., the degree of polymerization: also the amount and nature of the associated foreign matter. Harries' work on the ozonides of rubber shows the hydrocarbon to be an unsaturated body with two ethylene linkages. By bubbling ozone through a solution of rubber in chloroform, an ozonide  $-C_{10}H_{16}O_6$  (soluble in  $CHCl_3$ ) is formed.



The **formula I** indicates that rubber is an 8 carbon ring compound with two double bonds and that there are two methyl groups attached to the ring. The systematic name for the rubber hydrocarbon is "1.5 dimethyl-cyclo-octadiene 1.5". The term "octadiene" signifies an 8 C ring with two ethylene linkages. The 1.5 at the end states the position of the bonds in the ring whilst the 1.5 at the beginning of the expression refers similarly to the methyl groups. The compounds of the rubber hydrocarbon are addition products (except the nitrosite),  $C_{10}H_{16}O$ ,  $C_{10}H_{16}S_2$ ,  $C_{10}H_{16}Br_4$ , etc.

Rubber is a **colloid**, and is not, strictly speaking, soluble: it forms pseudo-solutions (swellings). A colloid is represented by suspended particles which, by carrying like (+ or -) electrical charges, repel one another continuously, and thus refuse to settle



by gravity. The addition of an electrolyte neutralizing the electric charges causes the particles to coalesce (coagulation), whereupon they settle out. A colloidal solution appears as a united mass of particles which, on greater dilution, decrease in size, disappearing to form a "sol," apparently limpid, although the beam of light employed in the ultramicroscope discovers solid particles. The first effect of the "solvent" is to swell the polyprene, forming a network or sponge. When the whole of the rubber is "swollen," diffusion of the solvent takes place.

The principal *rubber solvents* are carbon disulphide, turpentine, petroleum, benzene and its homologues, carbon tetrachloride and chloroform.

## EXAMINATION OF RAW RUBBER

The following information concerning a consignment of rubber might be required:

1. Origin, botanical source, method of collection, method of coagulation, despatch and packing.
2. The gross weight of shipment at the time of despatch, gross weight at the time of sampling, average tare, condition of the packages at unloading in dock.
3. The method of sampling is an important point to be decided between buyer and seller.
4. The washing loss, the content of washed dried rubber, and its appearance, color and strength after removal from the vacuum pans.
5. The percentage nitrogen content of the dried rubber, the percentage of acetone extract, percentage of ash.
6. Quantity of rubber (pure).
7. Results of trial vulcanizations.

## Raw Rubber

**Raw Rubber** (wild and plantation) appears on the market as sheets, blocks, slabs or scraps. Each kind of rubber possesses a characteristic odor due to the contained resin, decaying protein matter, or the material used in coagulation. The vegetable refuse, earthy impurities, moisture and soluble matter (organic acids, carbohydrates, tannins) may together constitute more than 50 per cent of the whole, which the process of washing and drying removes (residual moisture about 0.5 per cent). Plantation rubber is more carefully prepared and arrives clean, and being comparatively dry (as sheet, crêpe, or blocks) requires little or no washing. Purified raw rubber has a density of 0.91–0.97. It is highly elastic but loses its elasticity at 0° C. or if heated above 60° C. It melts at 100° C. to a black liquid.

**Technical analysis** of crude rubber (for factory control and valuation) consists in the estimation of washing loss, true rubber, resin and ash. The **sampling** of crude rubber is difficult because the packages differ greatly. If the bales are very heterogeneous the whole consignment should be washed and dried, as hand samples are quite unsatisfactory. The washing loss should be ascertained by weighing the whole shipment (or at least one-quarter of it) in batches of about 1 cwt., subtracting the tare, washing the rubber (preferably in presence of representatives of buyer and seller), weighing the vacuum-dried rubber after removal from the vacuum driers, and calculating the percentage of loss in each drier and taking the average. Determine "total insoluble" in hot pyridine.

**Laboratory samples** should not be less than 20 lbs. One sample should be

taken from each case, unless the packages are many and are much alike, when every third or fifth package may be sampled. In this case, wash and dry samples from the first half of the range and compare with results from the other half. If these results are within 1 per cent, take the mean. By using a long-bladed knife or toothless saw a wedge-shaped sample, having its apex at the center, may be cut, or in the case of a prismatic block the best sample may be obtained by cutting out a quarter. A slice through the center is obviously "against the seller." It is sometimes found that the rubber contains so little moisture or is so tacky that cutting is very troublesome. In this case the knife must be wetted and the superfluous water removed afterward, otherwise serious error will be caused if the small samples be taken.

**Tackiness.** Tacky rubbers always show a low state of colloidal aggregation compared with sound rubbers of the same species—their viscosity is also low. As they give the same figure on bromination, the tackiness is not due to oxidation or chemical change, but may be a physical degradation due to sunlight, heat, bacteria and enzymes, absence of moisture or presence of excessive moisture. Guayule is very susceptible, depending on its preparation and overheating during stowage in transit. The use of antiseptics in the wash water does not prevent tackiness, but Spence says that bacteria may be responsible for producing a condition in rubber favorable to tackiness. Morton has isolated an enzyme which will produce tackiness even in fine hard Pará. The chemicals used in coagulation may cause the condition—Spence considers sulphuric acid is inimical, also other mineral acids. Organic acids give hard and brittle rubbers. In any case strong coagulants produce the best rubbers. Antiseptics are advisable and cleanliness essential; overheating in drying rooms and ships is to be guarded against, and sunlight is to be avoided.

**Commercial evaluation** does not depend on chemical analysis alone. Physical tests and vulcanization trials (open and press cure, time and temperature and mixing variation) must be considered. Valuable information may be acquired by curing with 10 per cent sulphur, at 45 lbs. steam pressure, and withdrawing samples at certain intervals of time. The object of analysis is to assist the manufacturer in factory control and improvement of the manufactured articles, and to serve as a guide to the value and adaptability of the raw material.

Besides ordinary equipment, the *factory laboratory* should be provided with a small washing mill and vacuum drying oven, a mixing mill, centrifuge, Soxhlet extractors (fitted as usual) preferably with ground-glass joints. Talc baths are better than water baths (absence of steam). Cork connections should not be used for acetone extractions. A small muffle furnace, a crucible furnace and a small tube furnace will be useful.

### Analysis of Crude Rubber

**Chief Determinations.** Moisture, resin (acetone extract), insoluble, nitrogen, ash, rubber, traces of coagulant.

**Moisture.** Place 10 grams of rubber (cut into the smallest pieces possible with a pair of scissors) into a flat porcelain dish and dry the material in a vacuum oven for two hours at 50° C. (apply vacuum gradually). Estimation may be made in an ordinary air oven heated at 80° C. for three hours or until weight is constant, or the moisture may be determined by difference (after extraction with acetone). Original weight of rubber – (extract + residue) = moisture. Determination of moisture by desiccation *in vacuo* in presence of conc.  $H_2SO_4$  is a refinement for research purposes.

**Resin** (acetone extract). Two 3–5 gram samples from the washed and dried



the muffle. The ash of washed "plantation" ranges from 0.1–1.5 per cent. If white or pale yellow, and infusible—silica, lime, and magnesia are indicated. If highly ferruginous the ash is of a brick-red color.

Having determined the moisture, resin, ash and dirt, the rubber may be calculated by difference.

**Resins containing rubber** from Borneo, Sumatra and Malay (Jelutong, Pontianak, Dead Borneo), are used in vulcanized and unvulcanized rubber compositions, also in cements and chewing gum. These rubber-bearing resins should be examined for moisture (a 50 grams sample is heated *in vacuo* at 95° C.), dirt, resin (rubber by difference). The resins are hard and crystalline. Resin is determined by extracting a 2-gram strip rolled in filter paper, or as particles loose in the thimble. After extracting for two hours the shrunken mass should be again cut up and re-extracted.

**Insoluble.** Take 1 gram original or washed, dry rubber (if sticky), or use the residue from the acetone extraction if the rubber is firm.

(a) Weigh out 25 grams of washed, dried rubber and mix on the rolls. To 2 grams of this in a flask add 10 cc. toluene and heat for two hours under a reflux-condenser upon a talc bath. Allow to settle and filter, or better, centrifuge for one half-hour. Pour off the supernatant liquid, add more toluene and whirl again. The compact insoluble is received on a tared ashless filter. Weigh residue (1), incinerate and weigh (2), difference=organic insoluble. (Caspari.)

(b) Heat 1 gram of the finely divided sample in a large test tube with 10 cc. of phenetol for five hours. Allow to settle, filter, rinse on to a tared dish—dry and weigh. (Beadle and Stevens, I. R. Journal, 1912, p. 193.)

(c) Warm 2 grams of rubber with 15 cc. petroleum (B. P. 200° C.) in a small flask for one half-hour; dilute with 100 cc. benzene. Filter or centrifuge as in (a). (Caspari.)

**Protein. (Total Nitrogen).** Place 2 grams of the washed, dried rubber in a Kjeldahl flask with 30 cc. conc.  $H_2SO_4$  (or 20 cc. conc.  $H_2SO_4$ +10 cc. fuming  $H_2SO_4$ ) and one small drop (0.2 gram) of Hg. Loosely stopper the flask and heat over a naked flame, increasing heat gradually to vigorous boiling until the liquid is light straw-colored, and transparent (two or three small crystals of  $KMnO_4$  added towards the end will assist). Cool and dilute with water cautiously. Rinse into a 500 cc. flask, and add a solution of 2 grams sodium sulphide in 20 cc. water. Add 80 cc. NaOH solution (1.35) together with 0.5 gram Zn in small pieces. Connect for distillation and distill off the  $NH_3$  into a flask containing 20 cc. N/5  $H_2SO_4$ . Titrate the excess of N/5  $H_2SO_4$  with N/5 NaOH (using Methyl Orange as indicator). Calculate N, and multiply by 6.25 to obtain the weight of protein in the washed and dried rubber. N.B. Unwashed rubber contains substances rich in N. (See pp. 338 and 350.)

Wilfarth's modification of the Kjeldahl process is also recommended for the total nitrogen in rubber. It consists in digesting 1 gram of rubber with 30 cc. of conc.  $H_2SO_4$ , 7 grams  $K_2SO_4$ , and 1 gram anhydrous copper sulphate, for four hours and then proceeding as usual.

**Rubber.** For technical purposes it is sufficient to subtract the sum of the percentages of washing loss (moisture and dirt) ash, organic insoluble, and nitrogenous matter from 100 to obtain the percentage of rubber-hydrocarbon.

(a) **Spence's Method.** Take 1.5 gram acetone-extracted and vacuum-dried rubber. Add 100 cc. cold benzene. After swelling, make up to 200 cc.; mix and

filter through a tared funnel plugged with glass wool. Cover with a watch glass. Take 100 cc. of the filtrate in a tared flask, distill solvent, dry and weigh. Residue = pure soluble rubber. Calculate the percentage on the original weight. The remainder is diluted and filtered, washed with benzene and then with alcohol. Dry the residue at 65° C. and weigh. Residue = insoluble rubber + insoluble impurities.

(b) **Precipitation Method.** Weigh out 3 grams of material and swell in 10 cc. toluene, make up to 100 cc. with toluene, allow to settle (or use centrifuge). Into 100 cc. warm alcohol (95 per cent), transfer by means of a pipette 50 cc. of the supernatant liquid, stirring meanwhile. Remove the clot by means of a glass rod to another dish and redissolve in 100 cc. toluene. Reprecipitate in alcohol. Squeeze out the alcohol and transfer the clot to a tared watch-glass. Dry to constant weight (preferably *in vacuo*). Calculate percentage of rubber. If the rubber contains much resin use the acetone-extracted material.

(c) **As Tetrabromide: (Budde's Method, Spence and Galletly modification).** The value of this method is lessened by the fact that proteins and resins absorb bromine.

Dissolve 3 cc. Br and 0.5 I in 500 cc.  $\text{CCl}_4$ . Weigh out 0.2 gram of original rubber material. Extract with acetone. Place the residue in a wide-mouthed bottle, cover it with 50 cc.  $\text{CCl}_4$  and allow it to swell overnight. Add 50 cc. of the Br solution and allow reaction to continue six hours with the occasional shaking. Add 50 cc. alcohol with stirring, and wash the pptd. tetrabromide by decantation, with alcohol. Drain the ppt. and allow it to swell in  $\text{CS}_2$  (50 cc.). Reprecipitate the tetrabromide ( $\text{C}_{10}\text{H}_{16}\text{Br}_4$ ) by adding 50 cc. petroleum ether, wash with alcohol and dry below 60° C. Transfer ppt. to a porcelain crucible. Mix it with 4 grams of a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  (2 : 1). Gradually heat to redness. Dissolve the residue in distilled water, acidify with  $\text{HNO}_3$  and boil. Cool. Add excess of N/10  $\text{AgNO}_3$  and titrate excess of  $\text{AgNO}_3$  with N/10  $\text{AmCNS}$  sol., using Fe alum as indicator. Calculate Br.  $\text{Br} \times 0.42 = \text{rubber hydrocarbon}$ .

(d) **Nitrosite Method (Alexander).** Dissolve 1 gram of rubber (preferably acetone-extracted) in benzene contained in a weighed beaker. Pass nitrous fumes (from conc.  $\text{HNO}_3 + \text{As}_2\text{O}_3$  in small lumps, or starch) through a drying tower containing  $\text{P}_2\text{O}_5$ , and thence into the benzene-rubber solution for one hour, by means of a wide tube. Settle and decant the liquid through a weighed Gooch, and wash with benzene. Add 50 cc. fresh benzene, again pass the gas, and allow the beaker to stand overnight. Decant through Gooch, wash with benzene and with absolute ether. The beaker, tube and crucible are placed in the desiccator for one half-hour to remove ether. Dry in air oven at 80° C. Dissolve the nitrosite in acetone, and again dry and weigh the beaker and tube. The difference = rubber nitrosite.  $\text{R. N.} \times 0.47 = \text{rubber hydrocarbon}$ .

**Note.** For works-control, the ash, resin and washing loss must be determined upon every lot. The efficiency of the drying ovens must be tested after each operation—samples of the dried rubber being taken from several drying-pans and the moisture determined. The residual moisture should be less than 0.5 per cent. The soluble albuminoids are determined from the difference of N content of the unwashed and that of the washed rubber, the remainder being insoluble protein. (Caspari).

## FILLERS (Organic)

A rubber article may contain only 50 per cent rubber and sometimes much less. The *non-rubber portion* consists of a wide variety of substances, organic or inorganic. The *organic* fillers are generally substances of an oily, waxy or resinous nature. The *inorganic* fillers are finely-divided dry powders.

**Vulcanization** consists in the preparation of a dough containing essentially rubber, fillers and sulphur, and heating it at 125° C. to 175° C. for one to three hours, and the compounding materials are added (1) to impart desired effects (hardness, softness, pliability, strength, insulatory properties, resistance to chemical action), or (2) to give desired color, weighting or lightening the manufactured article, (3) cheapening, (4) modifying the vulcanization.

The *organic* diluents in common use are "Factice," reclaimed rubber and rubber waste, pitches (M. R. and coal-tar pitch), waxes, oils, petroleum residues, resins, dextrin, and cellulose. Factice, reclaim, waste and bitumen, cheapen the product. Waxes and oils are added for specific effect.

**Factice** is obtained by the interaction of glyceride-oils (linseed, cotton, maize, castor and rape) with sulphur chloride,  $S_2Cl_2$ , at 80° C. to 100° C., forming *white substitute*; or with sulphur alone at 160° C. to 180° C. yielding *brown substitute*. The product is a stiff jelly, insoluble in rubber solvents but swelling in them to form "gels." Factice is saponified by alcoholic alkali yielding glycerine and alkali soaps (both soluble in water). Factice is a complex mixture of factice proper, unvulcanized fatty oil, free sulphur and added impurities, such as paraffin wax, heavy petroleum, resin and bitumen.

For analysis of factice take samples from different parts of the consignment and thoroughly mix them upon the rolls.

**Moisture.** Dry 3 grams at 60° C. until constant in weight.

**Acetone Extract.** Weigh 2 grams into an extraction thimble, plug with cotton wool and extract with acetone. Dry the extract at 100° C. and weigh. The extract consists of unvulcanized oil, unsaponifiable matter and free sulphur. On cooling, paraffin wax, if present, will crystallize out and mineral oil will show fluorescence.

**Total Sulphur.** Add 2-3 grams of factice in small portions to 20 cc. conc.  $HNO_3$  contained in a porcelain dish. Allow reaction to continue in the cold for fifteen minutes. Gradually heat upon a water bath until the contents of the dish is reduced to a syrup. Add 5 cc. fuming  $HNO_3$  and evaporate again. Fuse the residue with KOH and a little  $KNO_3$ . Cool and dissolve in water. Precipitate the sulphur as  $BaSO_4$ . Calculate S.

**Sulphur in the Fatty Acids.** Saponify 10 grams of factice with alc. KOH. Decompose the soap produced with HCl. Collect the fatty acids, dry and weigh. Or after decomposing the soap with acid (HCl) warm upon a steam bath. Add 5 grams of pure, hard paraffin wax (correctly weighed) and allow it to melt with the fatty acids. Cool in a cold water-bath. Remove the cake and weigh after drying on blotting paper. Take an aliquot part of the fatty acids and determine the sulphur by a potash fusion (as above).  $Free\ S = total\ S - S\ in\ factice\ acids.$

**Saponifiable Matter.** Take two 2 gram portions of the mixed factice and extract with acetone as before. Add 50 cc. N. alc. KOH. Evaporate the alcohol and take up the residue with water. Transfer to a separatory funnel and shake out twice with ether. Evaporate the ether extract, and weigh. Total acetone extract - (free sulphur + unsaponifiable) = *unvulcanized oil*. The residue insoluble in acetone = factice proper.

Take 1 gram of the "residue from acetone" and make a nitrate fusion, or use the potash peroxide method. Gently heat in an iron basin with 10 grams of stick

KOH and add 10 cc. 95 per cent alcohol. Add 1 cc. water, heat and stir. Cool, and dissolve in water. Divide into two equal portions:

(a) Determine *sulphur* by adding excess of HCl, and BaCl<sub>2</sub> solution.

(b) Determine *chlorine* by adding excess of HNO<sub>3</sub> and AgNO<sub>3</sub> solution.

**Acidity.** Stir 5 grams of factice with 20 cc. alcohol. Total acidity is determined by titrating with N/10 NaOH, using phenolphthalein as indicator. Free sulphuric acid is sometimes present. Shake 5 grams of factice with hot water. Cool and filter, add HCl and precipitate with BaCl<sub>2</sub>. Express each acidity in terms of oleic acid. Total acidity (as oleic) - sulphuric acid (as oleic) = free fatty acid (as oleic), (in absence of neutral sulphates).

**Ash.** Incinerate two grams in the usual manner. Examine qualitatively.

Assay deliveries for acetone extract, free sulphur and unsaponifiable. Experimental mixings and vulcanization will determine the effect in manufacture.

### Bitumen and Pitch

**Asphaltum** is used in cable coverings to remove microporosity, and to increase insulation. Mineral rubber (M. R.) is a cheapening diluent and can be added in large proportions.

**Analysis. Asphaltene.** Soak 1 gram of the bitumen in 50 cc. cold petroleum ether for six hours. Crush with a glass rod and shake until disintegrated. Settle, filter, and wash the residue with petrol. The residue is known as the "asphaltene fraction." Dry and weigh. (a) Dissolve in benzene. Residue = mineral matter + carbon. Dry and weigh, (b)  $A - B = \text{asphaltene}$ . The solution in petrol, "petrolene" fraction, is brown and greasy, and may contain solid paraffin. If it is fluorescent and carbon is found in the residue, coal-tar pitch is indicated. (Caspari.)

**Softening Point of Bitumen and Pitches.** (Barta's modification of Kramer's and Sarnow's method.) Several pieces of glass tubing (6 mm. bore) are cut and ground true at both ends so as to be exactly 5 cm. long. Fill with melted and well-stirred bitumen. Cool and shave off surplus bitumen. Connect the tube by means of rubber to a similar but longer empty tube. Pour into the empty tube 5 grams of mercury. Fit the tubes into a test tube and heat in a bath of molten paraffin. Apply heat, increasing the temperature at the rate of 2° C. per minute. Note the temperature at which the Hg drops through. The softening point is generally 30° C. to 35° C. (Chem. Ind., 1903, p. 55.)

**Carbon in Coal-tar Pitch.** Dissolve 1 gram of pitch in 100 cc. hot benzene and allow to settle. Pour the supernatant liquid through a tared Gooch. Boil the residue again with 100 cc. benzene and filter: wash, dry and weigh.

Ceresine is soluble in hot acetone, but very slightly soluble in alcohol on cooling. Determine the M. P.; and acidity by N/100 NaOH; 20 grams should not require more than 1 cc. beeswax (used in ebonite), camphor, glycerin and resin should be looked for. All coloring matter used in the rubber industry should be examined for acidity. Pigments containing copper and chromium (examine ash) should be rejected. Paraffin wax and ceresine are used to reduce microporosity.

### Rubber Waste and Reclaim

Reclaim is prepared by grinding waste and treating it with water at high temperature in presence of acid or caustic alkali. Although reclaimed rubber contains its original combined sulphur it can be revulcanized. Regenerated rubber appears as a stiff dough and has not the resilience or strength of new material.



The following *determinations* should be carried out. Specific gravity, acetone extract, quantity of factice, quantity of factice in reclaim, etc.

Dry the "residue from acetone" and boil it in a small flask for three hours (under reflux) with 50 cc. of N/5 alcoholic KOH and pour off. Evaporate alcohol, boil with water, acidify and shake out with ether. Evaporate ethereal solution. Dry and weigh the residue (fatty acids). Multiply the weight of fatty acids by 1.1 to obtain the weight of *factice proper*.

$100 - (\text{percentage of extract} + \text{percentage of factice} + \text{percentage of ash}) = \text{percentage of rubber.}$

Reclaim should be examined for gritty matter and copper.

### Compounding Materials (Fillers and Modifiers)

The *most important* powders are: Litharge and white lead, zinc oxide, zinc sulphide, barytes, lithopone, antimony-sulphide, vermilion, ferric oxide, lime, chalk, magnesia, magnesium carbonate, kieselguhr, ultramarine, clay, mica, glass-powder and pumice. Consignments of these should be examined on arrival and checked with the sample. They must contain no injurious adulterants. (See present volume under separate heads for detection of impurities.)

All these materials should be in fine powdered form. Pass the powders through a sieve and examine for fragments of wood and metal. Determine *moisture* by drying 10 grams on Petri dish for two hours at 60° C. *Free mineral acid*, (where likely) is determined by boiling 5 grams of the material with distilled water filtering and titrating with N/50 NaOH. Calculate to  $H_2SO_4$ . This should be less than 0.1 per cent. Test for copper by AmOH.

**Rapid Method for the Determination of Inorganic Fillers (Mineral Matter, etc.) in Rubber Mixings.** Weigh out 1 gram of the sample. Extract with acetone and dry the residue at 50°-60° C. Heat it with 25 cc. petroleum B. P., 230°-260° C. in a 100 cc. Erlenmeyer flask in a paraffin-wax bath until the rubber has gone into solution. Fill the flask with benzene and allow it to stand for 24 hours to settle. Filter through a Gooch crucible which has been prepared by forming in it (over the usual two thicknesses of filter paper) a filter bed of kieselguhr of about half the depth of the crucible. Filtration is complete in 2 hours, a perfectly clear filtrate being obtained in one operation. The same filter can be employed again after removing the surface to a depth of two millimeters.

The litharge used should be completely soluble in  $HNO_3$  without effervescence. Objectionable impurities— $PbO_2$  (black flakes left in  $HNO_3$  solution) and copper. (See page 1184.)

Red Lead is used as an accelerator and may contain  $CaCO_3$  and  $Fe_2O_3$ . (See page 634.)

Test **Magnesia** for water of hydration, Ca and silica. Test for Mn and Cu. (See page 1292.)

**Barytes** should be pure white. Test for  $SiO_2$  and Fe. (See page 60.)

**Determination of Barium as Sulphate and Carbonate in Vulcanizing Rubber.** J. B. Tuttle (J. I. & E. Ch., 1916). The total Barium is determined as sulphate. To determine the  $BaCO_3$  weigh out into a porcelain boat 1 gram of rubber and place it in a glass tube and ignite in a current of  $CO_2$ . The finely ground residue is treated with 10 grams  $Am_2CO_3$ , 15 cc. strong ammonia and 50 cc. water. Boil 15 minutes to convert the Pb to carbonate. Filter off the insoluble  $BaSO_4$  and carbonates of Pb, Ba, Ca and Zn and wash the ppt. to remove the sol-



uble sulphates. Add 10 cc. glacial acetic acid and sufficient water to bring total volume to 100 cc. Heat to boiling. Filter. The Pb is removed as sulphide and the Barium is determined as carbonate. The Ba as sulphate is determined by difference.

Ultramarine may be present to disguise a yellow tint. (For analysis see page 1183.) Whiting ( $\text{CaCO}_3$ ) should be free from  $\text{SiO}_2$ , Fe and Mn. (See page 105.)

Silica must be white; determine moisture, ignition loss and bases. (Remainder = Silica.) (See page 1187.)

Dry 1 gram at  $110^\circ \text{C}$ . ignite, add HF and three drops of conc.  $\text{H}_2\text{SO}_4$ . Evaporate and ignite to oxides. (Loss =  $\text{SiO}_2$ .)

Talc is hydrated magnesium silicate. Test sample between finger and thumb for grit. Analysis should approximate to: Ignition loss 6 per cent, silica 60 per cent,  $\text{Al}_2\text{O}_3$  9 per cent,  $\text{MgO}$  25 per cent. (See page 293.)

Asbestos. Determine water of hydration,  $\text{SiO}_2$ , Fe and Mg. (See page 1187.) Rubber pigments may be tested by experimental mixing and vulcanization.

Zinc Oxide is completely soluble in 10 per cent acetic acid, without effervescence. Fe, Cu and Pb should be absent.

Lithopone is obtained by mixing BaS and  $\text{ZnSO}_4$  in molecular proportions and should therefore consist of an intimate mixture of  $\text{BaSO}_4$  (70.5 per cent) and 29.5 per cent  $\text{ZnS}$ . Determine soluble barium salts, soluble zinc salts, barium carbonate, moisture, acidity, insoluble, and total sulphide. (See page 1186.)

Antimony in Rubber Goods.<sup>1</sup> Three grams of the finely rasped rubber are treated in a Kjeldahl flask with 40 to 45 cc. of strong sulphuric acid. A small quantity of mercury or mercury salt is added, together with a small piece of paraffine wax. The mixture is heated until the rubber is dissolved and the black liquid begins to clear. Two to 4 grams of potassium sulphate are then added and the heating continued until a colorless or pale yellow liquid is obtained. After cooling, 1 to 2 grams of potassium metabisulphite are added and an excess of tartaric acid. The liquid is diluted sufficiently to prevent the charring of the tartaric acid and boiled until the odor of sulphurous acid has disappeared. A few cc. of dilute hydrochloric acid are added, the liquid diluted to 200 cc., filtered through a dry filter, and 195 cc. titrated either with iodine or with potassium bromate (the latter in acid solution), as described under the volumetric procedures, 21, 25.

Zinc sulphide is liable to contain  $\text{ZnO}$  as impurity. (Page 597.)

Determination of Zinc Sulphide. Take average sample and dry 5 grams for moisture; weigh 0.2 gram into a stoppered bottle, and shake with 50 cc. N/10 iodine solution. Add 5 cc. conc. HCl and allow bottle to stand two hours with occasional shaking. Titrate excess of iodine with sodium thiosulphate. One gram I = 0.384 gram.  $\text{ZnS}$ . (See also page 605.)

Antimony Sulphides. Crimson  $\text{Sb}_2\text{S}_3$  (prepared by boiling  $\text{SbCl}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$ ). Orange (by boiling powdered stibnite with polysulphides and precipitating the sulphantimonate with mineral acids). Plastered antimony contains 30-50 per cent  $\text{CaSO}_4$ . Antimony sulphide is tested for free sulphur, Sb,  $\text{CaSO}_4$  and sulphide-sulphur. Free sulphur: Extract 2 grams with  $\text{CS}_2$  (freshly distilled); drying extract at  $60^\circ \text{C}$ . Expel solvent from residue in thimble and dissolve  $\frac{1}{4}$  gram in conc. HCl, boil, add 2 grams tartaric acid and 150 cc. distilled water. Filter and weigh siliceous residue. Pass  $\text{H}_2\text{S}$  and determine Sb gravimetrically or volumetrically. (See page 21.)

<sup>1</sup> The Original procedure may be found in Chem. News, Vol. XXI, p. 124.

**Approximate rapid methods:**

(1) Heat in porcelain crucible 1 gram with  $\text{HNO}_3$  (1.4) and ignite. Residue =  $\text{SbO}_2 + \text{CaSO}_4$ .

(2) Mix 1 gram with 2 grams pure  $\text{AmCl}$  in a porcelain crucible, ignite ( $\text{SbCl}_3$  is volatilized). Residue =  $\text{CaSO}_4 + \text{Silica}$ . Total S by ignition with  $\text{HNO}_3$ , etc.

**Rouge.**—Determine Fe by boiling 0.5 gram with 500 cc.  $\text{HCl}$  (1.20). Add  $\text{AmOH}$ . Filter, ignite and weigh. Add  $\text{HF}$  and  $\text{H}_2\text{SO}_4$ . Ignite and weigh (loss = silica). Divide the filtrate into two equal parts and determine Ca and  $\text{SO}_4$ . (See page 247.)

**Vermillion** should contain no free sulphur, ash, soluble Hg salts nor aniline dyes. (See page 1192.)

**Lampblack.** Test for grease by extracting 2 grams with acetone. Ignite 2 grams for ash or shake 2 grams with acetone in 100 cc. flask, make up to 101 cc. Add 1 drop dil.  $\text{HCl}$ , allow to settle and pipette 50 cc. into a tared flask. (See page 1196.)

In **bone-black** determine amorphous carbon, calcium phosphate and calcium carbonate. Carbon is determined by dissolving out the mineral matter with  $\text{HCl}$ . Ignite residue and deduct ash.

**Magnesium Compounds.** French chalk (silicate of Mg). Determine moisture, ignition loss, magnesium carbonate and oxide. Find sp. gr. and degree of fineness by flotation method. Determine  $\text{CO}_2$  in Schroetter apparatus. (See page 124.)

**Lime** is used as a hastener of vulcanization. Determine  $\text{CaO}$  in presence of carbonate by dissolving out with a solution of cane sugar. Estimate  $\text{SiO}_2$ , carbonate, Mn, and Cu.

**Zinc Compounds** generally are tested for  $\text{ZnSO}_4$ , Pb, Fe. Estimate Zn by Ferrocyanide method. (See page 603.)

"**Flowers of Sulphur**" is obtained by sublimation. It contains moisture and free  $\text{H}_2\text{SO}_4$  (determine by shaking 10 grams with 20 cc. alcohol neutral to Phenolphthalein: Filter and titrate with  $\text{N}/10 \text{ NaOH}$ ). Maximum acidity allowable = 0.2 per cent. There should be no residue on ignition. (See page 519.)

**Sulphur chloride** distills between  $130^\circ$  and  $140^\circ \text{C}$ . Maximum residue = 5 per cent and consists of sulphur. Determination of Cl and S (**Weber's Method**). Weigh 5 grams  $\text{S}_2\text{Cl}_2$  into a 100-cc. flask, shake with benzene 100 cc. Pipette 10 cc. into 25 cc. N. alcoholic  $\text{KOH}$ . Digest on water bath for one hour. Distill solvent and dry at  $100^\circ \text{C}$ . Add 100 cc. hot water and two drops of  $\text{HNO}_3$ . Add 10 cc. of 10 per cent  $\text{CuSO}_4$  solution, filter and determine Cl by Gay-Lussac or Völhard method. Chemically pure  $\text{S}_2\text{Cl}_2$  contains 52.5 per cent Cl. (See also page 149.)

### Examination of Solvents

**Solvent naphtha** is the xylene fraction of coal-tar spirit and 95 per cent of it distills between  $125^\circ \text{C}$ . and  $150^\circ \text{C}$ . 90 per cent benzene is so called because 90 per cent of it distills below  $100^\circ \text{C}$ . Similarly with 50 per cent benzol.  $\text{CS}_2$  as an impurity in naphtha is estimated thus: Add 1 cc. phenylhydrazine to 100 cc. naphtha—allow it to stand one day. The crystalline deposit (the phenylhydrazine salt of phenyl-thiocarbazidic acid) is filtered off and weighed. Multiply by 0.26 for  $\text{CS}_2$ .  $\text{CS}_2$  (B. P.  $46^\circ \text{C}$ ; sp. gr. = 1.27) should not have an offensive odor. The distillation residue should be less than 1.5 per cent. Detection and determination as above. (Caspari.)

$\text{CCl}_4$  (B. P.  $77^\circ \text{C}$ . sp. gr. 1.63) should leave no residue on distillation.

### Vulcanized Rubber

**The properties of manufactured rubber** vary with the contents and vulcanization process. Oxygen or air causes the rubber to be hard and brittle especially in the case of low grades. Free  $\text{H}_2\text{SO}_4$  and traces of copper increase the tendency to oxidation. Light also favors the change and sunlight increases the acetone extract (degradation of rubber to resins). Soft rubber is stable towards dilute acids and alkalis. Rubbers containing  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{ZnO}$  are affected by acids. Strong  $\text{H}_2\text{SO}_4$  chars rubber and  $\text{HNO}_3$  oxidizes it.

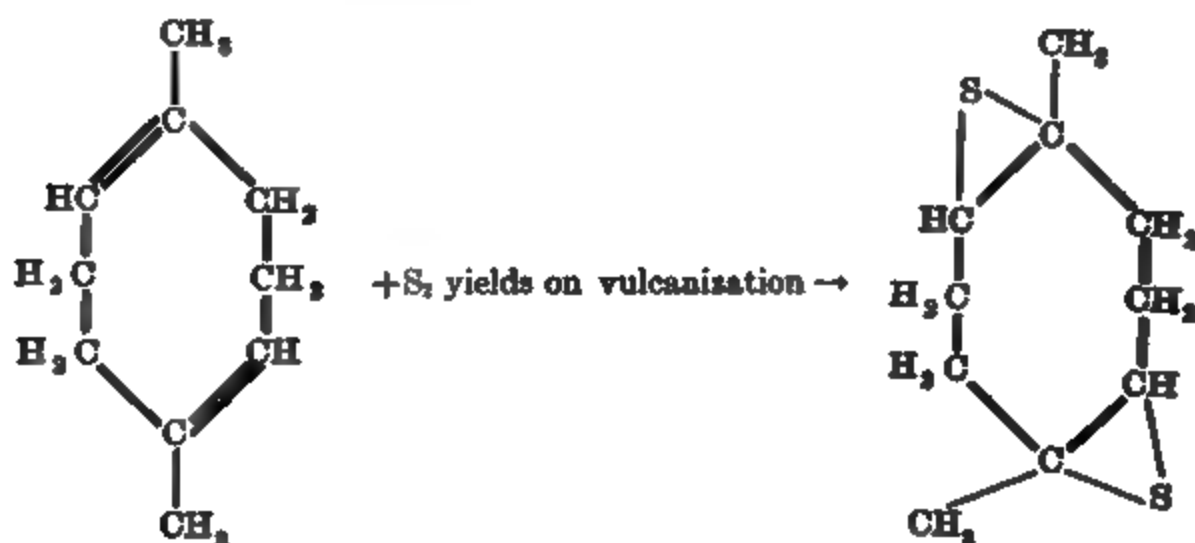
**Specific Gravity of Rubber.** Introduce into a pycnometer 5 grams of the rubber, cut into small pieces (not ground). Take care that no air bubbles are included. Calculate sp. gr. (water at  $15^\circ \text{C.} = 1$ ).

The most important physical properties of vulcanized rubber are stability to change of temperature, impermeability to water and gases, electric insulation. Well-vulcanized rubber absorbs very little water at ordinary pressure but gutta-percha is preferred for deep-sea cables under high pressure. Permeability to gases (N=1000, standard) CO 1113, air 1149,  $\text{CH}_4$  2148, O 2556, H 5500,  $\text{CO}_2$  13,580. From these figures it is seen that diffusion is supplemented by another action—adsorption (Ditmar). Paraffin lessens the permeability. Rubber is inferior to gold-beater's skin for balloons. In presence of oxygen, ultra violet light has a less effect upon vulcanized rubber than on the crude substance. A chrome-yellow ultra-violet light screen is used for balloons.

Vulcanization was introduced by Goodyear, 1839, who secured no patent until 1844. Thos. Hancock, in 1843, patented a process in England; Parkes in 1846. The use of molds in curing was introduced by Hancock in 1846. Hollow goods were first made by Goodyear in 1848 and ebonite in 1851.

**Chief Methods of Vulcanization.**—1. Heating with sulphur, with or without sulphur carriers, such as lead compounds, either in hot air by means of steam and pressure.

2. Cold cure, by means of sulphur chloride dissolved in  $\text{CS}_2$ . Cold-cured goods contain chlorine as well as sulphur. The change from rubber hydrocarbon to ebonite is probably represented by the following formulae.



The amount of combined sulphur depends upon the amount of sulphur introduced, the temperature, and time of vulcanization.

$$\text{The coefficient of vulcanization} = \frac{\text{sulphur of vulcanization}}{\text{rubber substance}}$$

Wo. Ostwald is of opinion that the process is adsorption, giving a whole series of sulphur-additions, the members of which have not yet been isolated.

**Analysis of Vulcanized Rubber. (Manufactured goods)**

**Sample and its Preparation. Sampling for analysis.** If the material is hard: ebonite raspings and shavings are well mixed or the ebonite is broken up by slowly grinding in a small coffee-grinder. Soft rubbers should not be worked on the mill, as they heat up (increase in acetone extract). They may be broken up by passing through a household mincing machine. A good sample is obtained by selecting representative portions and cutting these with scissors into the smallest possible particles. The *object of analysis* is the detection or control of constituents, and may comprise the following *determinations*: Moisture, ash, acetone extract, free sulphur, total sulphur, alcoholic potash extract.

**Acetone extraction** removes free-sulphur resins, oils, waxes, mineral rubbers and substitutes. Soft rubber requires at least eight hours and ebonite two days for extraction. The process may be hastened by digesting with acetone at 100° C. in a sealed bottle.

Make two extractions on 2-gram samples and treat as in the case of crude rubber. If the acetone extract is fluorescent the presence of coal-tar pitch is indicated. A yellow-colored extract indicates bitumen. On cooling, crystals of sulphur or paraffin wax may appear.

Unite the two extracts and add 50 cc. alc. KOH (almost colorless). Boil under reflux for two hours. Distill the alcohol. Heat the residue with 10 cc. distilled water, cool somewhat and add ether (20 cc.). Shake until waxes, etc., are in solution and transfer the whole to a separator; wash out the flask with ether and warm water. Shake and allow the contents to separate. Draw off the aqueous solution into another separatory funnel, leaving the flocculent portion in the first separator. Add pure ether to the second funnel and unite ether layer with ethereal layer in first funnel. Filter the ethereal portion (through small plug of cotton wool) into a weighed flask. Evaporate the solvent, dry at 100° C. and weigh the unsaponifiable matter in the acetone extract. (Reserve this residue for estimation of hydrocarbons,—paraffin.) The unsaponifiable residue from the alcoholic KOH may contain hydrocarbons and unsaponifiable resins. The resins, and part of the hydrocarbons are soluble in alcohol and may be thus estimated:

Add 3 cc. conc.  $H_2SO_4$ , cover, and heat for four hours at 110° C. in an air oven. Cool, and add 30 cc. petrol. Boil under reflux for one hour. Pour off the petrol portion carefully into a separator, wash it with 15 per cent KOH to which an equal volume of alcohol has been added. Draw off the petrol solution and evaporate it in a tared flask. The increase in the weight of the flask—hydrocarbon (paraffin wax or mineral oil). The aqueous portion in the separatory funnels contains the free sulphur and the saponifiable part of the acetone extract (as potassium salts). Evaporate the aqueous liquid to small bulk, transfer it to a nickel dish, add 2 grams  $KNO_3$  and evaporate to dryness upon an asbestos card from which a convenient central hole is cut; heat to quiet fusion. Dissolve the melt in hot water, and transfer it to a porcelain dish. Acidify with HCl, evaporate to dryness and dehydrate in an air oven (150° C. for one hour). Add 2 cc. conc. HCl, take up with water, filter and wash. Bulk should be 200 cc. Boil and add slowly from a pipette a slight excess of  $BaCl_2$  10 per cent solution. Treat the  $BaSO_4$  in the usual manner. Calculate sulphur.

The free sulphur may be estimated directly upon the acetone extract.

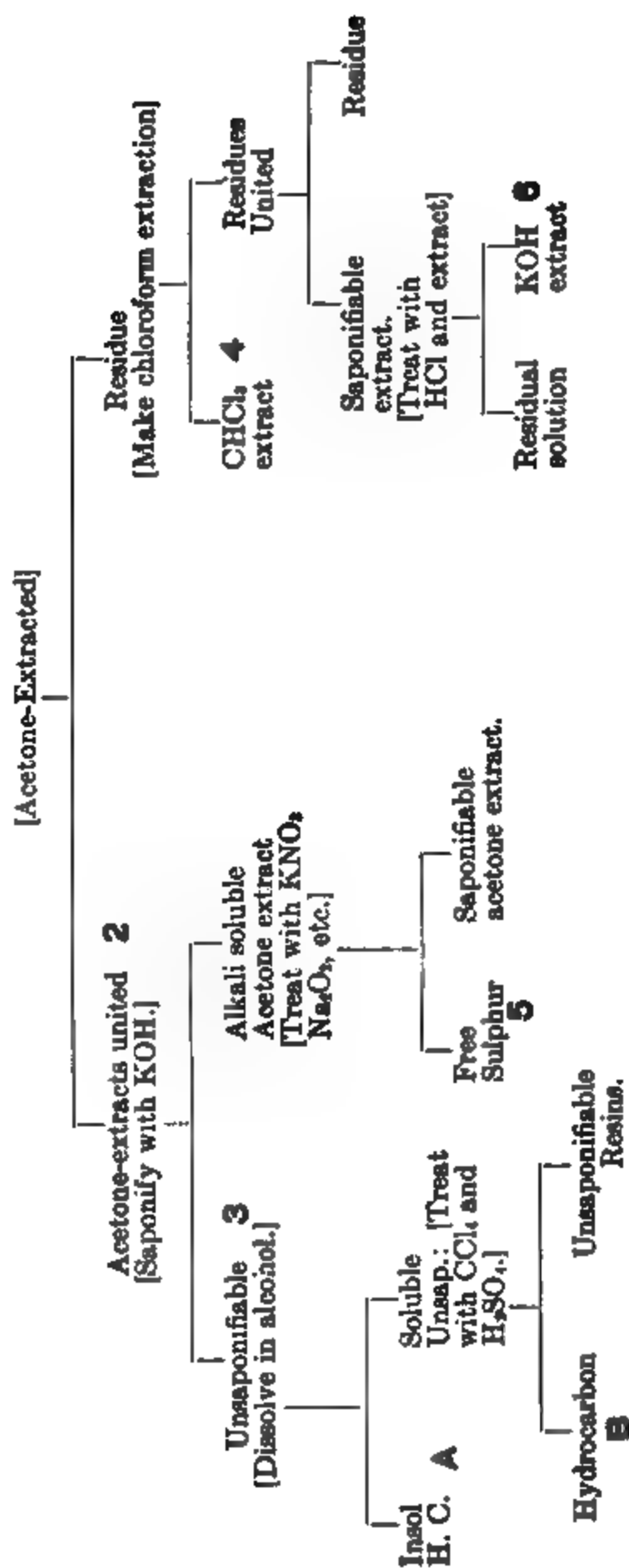
**Thiocyanate Method.**<sup>1</sup> To the acetone extract add 25 cc. 95 per cent alcohol and

<sup>1</sup> Davis and Foucar, J. S. C. I., 1912, p. 100.

# Joint Rubber Insulation Committee Method

## Outline

Two 2 gram samples of Rubber 1



[Total waxy Hydrocarbons A+B. Weigh substances ringed, others by difference.]

(See Jour. Ind. & Eng. Chem., Jan., 1914.)

a lump (1 gram) of KCN. Boil under reflux for half an hour. Remove excess of cyanide and boil off alcohol. The sulphur now exists as KCNS. Dilute and add 1 cc.  $\text{HNO}_3$  and a little Fe alum. Titrate with  $\text{N}/10 \text{ AgNO}_3$ . 
$$\text{S} = \frac{\text{Ag}}{0.297}$$

**Oxidation Method.** Heat acetone extract with 5 cc. conc.  $\text{HNO}_3$  and a little powdered  $\text{KClO}_3$ . Cover and heat on a hot plate for six hours. Dilute with weak  $\text{HCl}$ , filter and precipitate with  $\text{BaCl}_2$ . Test the original substance or the residue from the acetone extract with  $\text{CS}_2$ ,—a brown solution indicates bitumen or pitch. The acetone has removed part of the bitumen. If bitumen is indicated air-dry the residue, plug the thimble and extract with  $\text{CS}_2$  for six to ten hours. (Note: Vulcanized rubber is insoluble in  $\text{CS}_2$ ). Distill the solvents, and weigh the extract.

**The Residue from Acetone. (Chloroform Extraction.)** Extract with chloroform (60 cc.) for four hours. Distill the solvent and weigh the extract, which will contain that part of the bitumen (brown color) that was insoluble in acetone. Any uncured rubber present will be dissolved out by chloroform, although even a properly cured compound will yield a little extract to chloroform.

**Alcoholic KOH Extraction.** The residue from the chloroform extraction consists of rubber, factice and mineral charge. It is now boiled (in a flask fitted with a ground-in reflux condenser), with 50 cc. alc.  $\text{KOH}$  for four hours. Pass the solution through a filter, wash with absolute alcohol and subsequently with hot water. Evaporate the solution to a pasty condition to expel the alcohol. Take up with hot water and transfer the liquid to a separator. Acidify with dilute  $\text{HCl}$ , make up to 100 cc. with water, and allow the liquid to cool. Add 50 cc. ether and shake. Draw off aqueous solution and treat it with ether again. Unite the ether solutions in a separator and wash with water until the ether solution is acid free. Filter ethereal solution into a tared flask, washing the filter with ether. Allow the ether to evaporate gently. Dry the residue at  $95^\circ \text{C}$ . and weigh.

The residue in the flask consists of the free fatty acids of "factice." Multiply by 1.2 if  $\text{Cl}$  was found in the alc.  $\text{KOH}$  extract, or by 1.3 if  $\text{Cl}$  was absent.

The material left in the flask in which the saponification with alc.  $\text{KOH}$  took place consists of rubber-hydrocarbon, combined sulphur and mineral charge.

The coefficient of vulcanization involves three determinations:

1. Total combined sulphur.
2. "Inorganic" sulphur.
3. Rubber hydrocarbon.

The total combined sulphur is determined in the residue from the alc.  $\text{KOH}$  extraction.

**Henrique's Method.** Weigh out 1 gram of the material into a large porcelain crucible. Add 15 cc.  $\text{HNO}_3$ . Cover and gradually heat until evaporated. Add slowly 5 grams  $\text{Na}_2\text{CO}_3 + \text{KNO}_3$  (2 : 1). Heat until action starts, withdraw flame and cover the crucible. Heat to fusion and pour the melt into a beaker of water. Lixivate, filter and estimate  $\text{S}$  as  $\text{BaSO}_4$ . Reserve the residue for the determination of  $\text{Pb}$ ,  $\text{Zn}$ ,  $\text{Ba}$ ,  $\text{Mg}$ . (See pages 55, 271, 291.)

The coefficient of vulcanization = 
$$\frac{\text{S combined with rubber}}{\text{Rubber present}}$$

When no sulphur is present in the organic or mineral fillers the estimation is simple. The combined sulphur corresponds to the sulphur of vulcanization and equals "total sulphur—free sulphur." If substitutes are present, estimate the sulphur of vulcanization

on the dried sample after the alcoholic NaOH treatment and calculate the result on the original amount of rubber.

If mineral matter containing sulphur be present:

1. Estimate the combined sulphur and sulphur in the mineral matter after removal of rubber by kerosene. Difference = combined sulphur of vulcanization.
2. Separate rubber from the mineral by solution in xylene (under pressure).

Isolate the rubber from the solvent by distillation in steam. Then estimate the sulphur of vulcanization directly on the rubber. See J. S. C. I., 1911.

The isolation of the solid compounding materials is effected by means of petroleum. Take 2 grams of original, or equivalent amount of acetone-extracted material. Soak overnight in 10 cc. petroleum (B. P. 200° C.). Heat under reflux. Rinse the contents into a tube and centrifuge for half an hour. Pour off supernatant liquid and repeat with more petroleum. Weigh the residue, which consists of inorganic matter, starch, carbon, etc.

**Mineral Matter.**—Incineration may produce change in the mineral constituents.  $MgCO_3$  would lose  $CO_2$ ; some Sb and Hg compounds being reduced by carbonaceous matter would volatilize even at low temperature, and sulphides would gain in weight on oxidation to oxide or sulphate. Therefore ashing will give only approximate results. Incinerations should be slowly carried out at a low red heat. The vapors should not inflame. Take 1 to 5 grams according to sp. gr. of rubber and heat in a flat porcelain dish. Transfer the char to a muffle and burn off the carbon.

**Solvent Method.** Take the acetone-extracted material. Two grams are finely divided and covered in a 50 cc. conical flask with 10 cc. kerosene (B. P. = 200° C.). Soak overnight. Reflux on sand bath with frequent shaking for two hours. Cool and settle. Transfer to centrifuge tube and whirl. Pour off liquid (or siphon). Add fresh petroleum and centrifuge again; and weigh residue.

**Total Sulphur.** Weigh into a conical beaker 1 gram rubber and add 15 cc. fuming  $HNO_3$ , cooling under tap if necessary. Warm on a water-bath, transfer to a porcelain basin and evaporate twice with fuming  $HNO_3$  to a syrup. Mix with 5 grams of fusion-mixture and fuse. Lixivate and filter (if Pb or Ba is present). Acidify with HCl and evaporate. Add 5 cc. HCl and dissolve in water. Filter and add  $BaCl_2$ . Proceed as on page 341.

**Stevens' Method** for the determination of total sulphur in vulcanized rubber (Analyst 1918, 43) is as follows: Half a gram of the sample is digested with 20 cc.  $HNO_3$  (1.42) and 0.5 gram  $KClO_3$  is added. Boil for three hours under reflux condenser. Evaporate dry in a porcelain basin with the addition of 3 grams of magnesium nitrate. Heat residue cautiously over a naked flame. (The magnesium salt moderates the combustion.) Any unburnt carbon is destroyed by digestion with  $HNO_3$  and  $KClO_3$ . The excess of acid is expelled. Add 10 cc. strong HCl and cover the dish with a clock-glass. Gently heat until the red fumes cease to be evolved. Dilute liquid, filter, make up to 300 cc. Heat to boiling point and precipitate  $BaSO_4$  with 5 cc.  $BaCl_2$  sol. (10%). Allow to stand overnight and filter.

**Note on Total Sulphur:**

The Carius method is the most reliable, but it requires special apparatus. The rapid method of Kaye and Sharpe is carried out as follows: 0.25-0.5 gram of the finely divided sample is intimately mixed with 5 parts by weight of pure zinc oxide and four parts of  $KNO_3$  in a porcelain crucible and a thin layer of  $ZnO$  replaced on the surface. Cover the crucible and heat it gently until the reaction commences, when the





**AmCl.** Remove fatty matter by ether. Settle and pour the clear liquid through the original filter. Boil residue with AmOH and AmCl and filter again. Boil the residue with dilute HCl (100 cc.) and filter through the original paper. Wash, dry and weigh ( $=\text{BaSO}_4 + \text{CaSO}_4 + \text{carbon}$ ). Incinerate and weigh. Difference = carbon.

**Determination of Antimony and Mercury in Rubber Goods.** Heat 2 grams rubber with 20 cc. conc.  $\text{H}_2\text{SO}_4$  in a Kjeldahl flask. Boil for three hours. Cool, add 1 gram  $\text{KMnO}_4$  crystals gradually. Boil for ten minutes. Cool and take up with 300 cc. water. Boil and filter. Precipitate the Sb and Hg by  $\text{H}_2\text{S}$  and determine in the usual way if present alone. If together, collect the mixed sulphides on a tared filter; wash and rinse into a beaker. Warm with  $\text{Na}_2\text{S}$  solution. Filter and wash. Reprecipitate the Sb by HCl and determine as on page 251. The sulphide residue contains the Hg. Boil with HCl (1 : 1). Filter and pass  $\text{H}_2\text{S}$ . Collect the precipitate and add it to the  $\text{HgS}$  undissolved by the  $\text{Na}_2\text{S}$  solution. Wash with very dilute HCl, remove the water by alcohol,  $\text{CS}_2$ , dry and weigh. (Or use method on page 310.)

### Analysis of Mechanical Goods

**Acetone Extract.** Place 2 grams material in a paper thimble and extract with acetone for eight hours. Transfer the extract to a tared flask. Drive off the solvent and dry the flask at  $90^\circ \text{C}$ . in *vacuo*. (Acetone extract uncorrected.)

**Free Sulphur.** Add to the flask containing the acetone extract (uncorrected) 60 cc. distilled water and 3 cc. Br. Heat until colorless. Filter, and cover with a watch glass. Heat to boiling on a steam bath. Add 10 cc. of 10 per cent  $\text{BaCl}_2$  solution, and allow to stand several hours. Filter and treat the  $\text{BaSO}_4$  as usual.

**Total Sulphur.** 0.5 gram rubber is weighed into a porcelain crucible (100 cc.). Add 20 cc. nitric acid and bromine solution. Cover with a watch glass and allow the whole to stand for one hour. Heat gently, rinse the cover with distilled water and evaporate to dryness. Add 5 grams fusion-mixture together with 4 cc. distilled water. Digest for five minutes. Dry in a steam bath or upon a hot plate; fuse. Cool the crucible and place it in a large beaker. Cover it with water and digest. Filter the liquid and make up (with washings) to 500 cc. Add excess of HCl and heat. Precipitate with  $\text{BaCl}_2$ , etc.

**Rosenstein's Method.** Weigh exactly 0.5 gram of the ground sample into a 300 cc. Erlenmeyer flask. Add 15 cc. saturated solution of arsenic acid, 10 cc. fuming  $\text{HNO}_3$  and 3 cc. saturated Br water. Cover with a watch glass and boil until the sample is completely oxidized and a clear solution is obtained. Evaporate the liquid to a syrup. Add a few crystals of  $\text{KClO}_4$  to ensure complete oxidation, and to expel nitrogen oxides. Evaporate to dryness. Cool and take up with 50 cc. 10 per cent HCl. Heat until dissolved, filter and dilute to 300 cc. with distilled water. Precipitate with  $\text{BaCl}_2$  in the usual way.

**Ash.** One gram comminuted rubber is wrapped in filter paper and extracted with acetone for four hours. Transfer the rubber and filter to a porcelain crucible and ignite it at low temperature. Cool and weigh.

**Sulphur in Ash.** Add a few drops of  $\text{HNO}_3$  to the ash. Stir and expel excess of acid by heating on a water bath. Add 5 grams fusion mixture. After fusion treat the melt as usual. Barytes is calculated from the content of barium in the ash.

1. Subtract the free sulphur from the acetone extract, uncorrected.

2. Subtract the sulphur in the ash from the total ash to obtain "ash (sulphur-free)."

3. Subtract from the total sulphur the percentage of sulphur as barytes (total sulphur corrected). Add the sulphur so deducted to the ash, reporting the ash as "ash corrected."

4. Subtract from 100 the sum of acetone extract corrected, total sulphur, ash (sulphur free), and call the remainder "rubber by difference."

**Sulphide Sulphur. Stevens' Method.** The vulcanized rubber is first swollen in a suitable solvent in which the aqueous acid is partly soluble. By this means the  $PbS$  and  $ZnS$  are decomposed. The solvent used is methylated ether. The liberated  $H_2S$  is estimated and calculated to percentage of sulphide sulphur, by absorption in lead acetate solution.

Twenty cc. conc.  $HCl$  and 30 cc. methylated ether are placed in a Voigt's flask. Expel the air by a current of  $CO_2$ . Connect the flask to an absorption apparatus containing lead acetate solution. Introduce a weighed quantity of the rubber into the flask. The rubber swells gradually and after fifteen minutes the ether together with the evolved  $H_2S$  is driven over into the absorption apparatus by a gentle heat. Boil the mixture for ten minutes. Collect the  $PbS$ , wash and titrate with iodine. The residue in the flask is extracted again with  $HCl$  and the sulphate is determined as  $BaSO_4$ .

## GUTTAPERCHA AND BALATA

Guttapercha is obtained from the latex of certain plants belonging to the natural order Sapotaceæ, growing wild in the Malay Peninsula, Sumatra and Borneo. Balata is obtained from Venezuela and Guiana. The hydrocarbon present in guttapercha and balata is similar to that of rubber, but a larger proportion of resin is associated with the former. When cold the gutta hydrocarbon is hard and tough like leather, yet pliable, whilst elasticity is almost entirely absent. On warming guttapercha and balata they soften and become plastic. Guttapercha is used chiefly for cable coverings, surgical and chemical utensils, whilst balata is used chiefly for belting. Although guttapercha and balata can be vulcanized their value is not thereby increased. Therefore the material is used after it is merely washed and dried. No compounding materials are added, but the material is sometimes deresinated in order to produce harder mouldings.

**Sampling.** The only satisfactory way to arrive at a washing loss of a parcel of guttapercha is to wait until the whole of the consignment has passed through the washing mills and drying ovens and then to calculate the shrinkage from the yield of the washed and dried material. The shrinkage ranges from 25 per cent to 50 per cent.

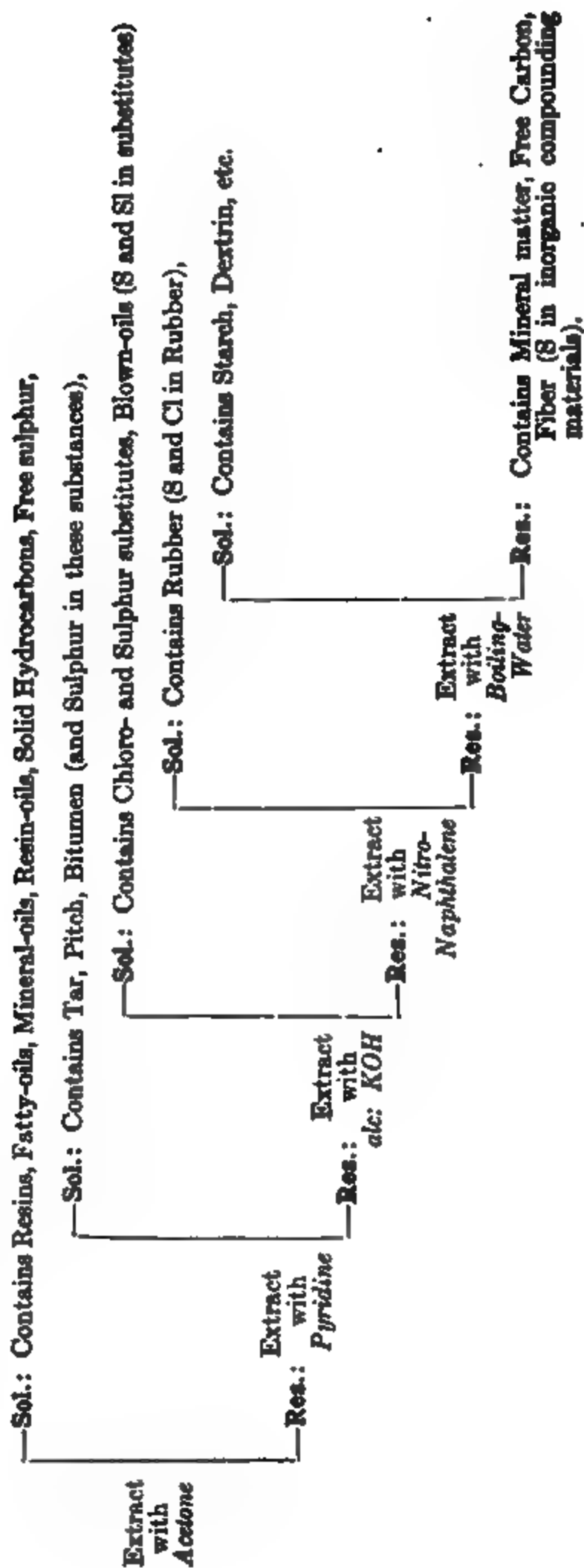
**Analysis.** Determinations required: Moisture, resin, dirt, gutta hydrocarbon.

**Moisture.** Weigh out 3 to 5 grams of the material reduced to small particles, and dry it on a flat dish *in vacuo* at  $90^\circ C$ . for six hours, or heat the guttapercha in a current of dry  $CO_2$ .

Acetone is the most trustworthy solvent for the extraction of balata and guttapercha. Ether dissolves a part of the gutta or balata, and so gives high result; whilst with alcohol the gutta becomes plastic on account of the higher boiling point of the solvent, and the extraction is, therefore, incomplete.

**Resin.** Extract 2 grams of the finely divided sample with acetone, as in the case of rubber, for twelve hours. Evaporate the solvent and dry the residue to constant weight at  $110^\circ C$ .

**Gutta: Rapid Method.** Boil 1 gram sample with 20 cc. redistilled toluene. Heat to  $100^\circ C$ . on a water bath until dissolved. Pour the solution into 50 cc. 95 per cent alcohol. Allow the contents of the vessel to stand for a few hours.

*Alternative Scheme for Rubber Analysis:*

urn and agitate to clear the liquid. Remove the clot, redissolve in toluene and precipitate by alcohol. Dry *in vacuo* and weigh.

Dirt (generally less than 0.5 per cent) and mineral matter are determined incineration.

The *residue* may be examined for ZnO, lithopone, antimony sulphide and carbon.

The examination of *Balata* is conducted similarly.

*Works of Reference on Rubber: recommended, and to which acknowledgments due:*

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Methods of Analysis of Raw-rubber: Spence. *Quarterly Jour.*, vol. II, page 91.

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Die Analyse des Kautschuks, etc.: Ditmar.

# ANALYSIS OF EXPLOSIVES<sup>1</sup>

C. G. STORM<sup>2</sup>

The methods described in this chapter cover all of the more common types of explosives employed in the United States for both commercial and military purposes. Those of chief commercial importance are black powder, nitro-glycerin dynamites, including "straight" dynamites, ammonia dynamites, gelatin dynamites, and low-freezing dynamites, "Permissible" coal mining explosives and nitrostarch blasting explosives. Military explosives include smokeless powder, guncotton, trinitrotoluene, picric acid, ammonium picrate, "Amatol," tetryl and tetranitroaniline. No sharp distinction can, however, be drawn between commercial and military explosives, as many are utilized for both purposes. Many tons of surplus TNT. have been used recently in commercial work; nitrostarch explosives found important application for military use during the war; mercury fulminate and other detonators and priming compositions are essential in every field of explosives.

The methods described have largely been used by the writer in practical explosives testing and analysis in connection with both Government and private work. Most of those applying to commercial explosives have been approved by the United States Bureau of Mines for use in its Explosives Chemical Laboratory.<sup>3</sup>

## BLACK POWDER

The composition of black powder varies to some extent, depending chiefly on the purpose for which the explosive is to be used. Black blasting powder contains sodium nitrate, charcoal and sulphur; black gunpowder is quite similar except that potassium nitrate is generally substituted for the sodium nitrate; black fuse powder is similar to the latter, differing mainly in its granulation. The same general method of analysis is therefore applicable to all types of black powder.

**Sampling.** From 50 to 100 grams of the original sample is crushed in small portions in a porcelain mortar and completely passed through an 80-mesh sieve, care being taken to avoid undue exposure to the air. The separate powdered portions are promptly bottled and the entire sample is finally well mixed.

**Moisture.** The standard method of the Bureau of Mines is to desiccate a 2-gram sample on a 3-inch watch glass over sulphuric acid for three days, the loss of weight being moisture. It has been shown, however, that equally accurate results can be obtained by drying at 70° C. in a constant temperature oven to constant weight, for which 2-3 hours is usually sufficient. As much as 5 hours drying at 70° C. will not cause loss of sulphur. Drying at 100° C. gives results which are slightly high, due to loss of sulphur.

<sup>1</sup> Received March, 1920. Published by permission of Chief of Ordnance, U. S. A.

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<sup>3</sup> See Bureau of Mines Bulletin No. 51, "The Analysis of Black Powder and Dynamite," W. O. Snelling and C. G. Storm, 1913, and Bulletin No. 96, "The Analysis of Permissible Explosives," C. G. Storm, 1916.

**Nitrates.** About 10 grams of the finely ground sample in a Gooch crucible provided with an asbestos mat, is extracted with warm water by means of suction, the water being added in 15–20 cc. portions and each portion being allowed to stand in the crucible a short time before suction is applied. About 200 cc. of water is usually sufficient, but the last drops of filtrate should be tested by evaporation to ensure the absence of nitrates. A blue color on the addition of sulphuric acid containing a few crystals of diphenylamine will also indicate the presence of nitrates.

The water extract includes a small amount of water-soluble organic material from the charcoal in addition to the nitrate. It is made up to 250 cc. and an aliquot portion (50 cc.), evaporated to dryness on the steam bath, treated with a little nitric acid, again evaporated, heated to slight fusion and weighed.

If allowance for impurities in the nitrate is desired, a direct determination of nitrate may be made on a separate portion of the water extract by the Devarda method or by means of the nitrometer, but for all practical purposes the evaporation method is sufficient. The usual tests should be made to determine whether sodium nitrate or potassium nitrate is present.

The residue left in the crucible, consisting of sulphur and charcoal, is dried at about 70° C. to constant weight (for 5 hours or over night if more convenient), the loss of weight minus the moisture content being the water-soluble portion. This result serves as a check on the evaporation result.

**Sulphur.** The residue in the crucible is extracted in a Wiley extractor or other continuous extraction apparatus with carbon disulphide, until evaporation of a small portion of the solvent passing through the crucible shows absence of sulphur. The excess of carbon disulphide is then allowed to evaporate from the crucible in a warm place away from flame, and the residue finally dried to constant weight at 100° C. The loss of weight is considered as sulphur.

**Charcoal.** The dry residue in the crucible should consist only of charcoal.

**Ash.** The ash in the charcoal may be determined by ignition over a Bunsen burner until all of the carbon has been burned off, and weighing. This ash also contains, of course, any non-volatile matter that may have been present in the sulphur and nitrate.

**Calculation of Results.** Since a portion of the charcoal is always dissolved in the water extract, it is customary to express the content of charcoal by subtracting the sum of the following from 100%:

% Moisture (by desiccation or drying at 70° C.).

% Nitrate (by evaporation of water extract with  $\text{HNO}_3$ ).

% Sulphur (by loss on extraction with  $\text{CS}_2$ ).

## NITROGLYCERIN DYNAMITES

## "Straight" Dynamite

So-called "Straight" nitroglycerin dynamite has been manufactured to only a relatively small extent in this country during the past few years, owing to the high cost of glycerin. It has been largely replaced by the ammonia and low-freezing dynamites, in which a large part of the nitroglycerin is replaced by ammonium nitrate and nitrosubstitution compounds. Furthermore, developments in the manufacture of both ammonium nitrate and nitrocompounds during the war have rendered unlikely any great increase in the manufacture of straight dynamites. They are still largely used, however, where quick-acting blasting explosives of high strength are required, as in work in hard rock. They consist essentially of nitroglycerin absorbed in a "dope" composed of a combustible absorbent, usually wood pulp, and an oxidizing material (sodium nitrate), to which is added a small amount of an antacid (calcium carbonate, zinc oxide, etc.). The analysis is best carried out by successive extractions, usually with ether, water, and dilute hydrochloric acid.

**Sampling.** The wrappers are removed from a number of the cartridges, and from 3 to 5 cm. of the ends of the exposed roll of explosives rejected. The remainder is thoroughly mixed on a large sheet of paraffined paper or in a large porcelain dish, and an average sample selected and bottled—usually about one half pound. The importance of thorough mixing of the sample must not be overlooked, in view of the fact that there is frequently a decided tendency for the nitroglycerin to segregate due to insufficient or unsuitable absorbent, so that this liquid ingredient may not be uniformly distributed throughout the cartridge. Also if a carefully mixed sample has been allowed to stand for some days, especially in a warm place, segregation may occur in the bottle, so that it is advisable to again mix the sample before analysis.

**Qualitative Examination.** Although a qualitative analysis of a sample known to be straight nitroglycerin dynamite is usually unnecessary, the exact nature of the sample may be unknown, and a knowledge of the composition of some of the more complex types of dynamite is necessary before a quantitative analysis can be properly conducted.

About 25 grams of the sample is shaken with several successive portions of ether in a large stoppered test tube, the ether being decanted off through a filter paper and the residue finally washed on the filter. The ether solution is allowed to evaporate slowly on a steam bath and the filter paper spread out on a glass plate in an oven so that the residue may dry quickly. The evaporated ether extract may contain nitroglycerin, sulphur (especially in the lower grades of dynamite), rosin, vaseline, or paraffin oil (in ammonia dynamite), nitrotoluenes and other nitrocompounds (in low-freezing dynamites), etc.

Nitroglycerin is readily detected by shaking a drop of the liquid with one or two cc. of strong  $H_2SO_4$  and about 1 cc. of mercury in a test tube, an evolution of brown fumes of nitric oxides being noted if nitroglycerin is present. Sulphur will appear as crystals in the evaporated extract, and may be identified by removing them, washing with acetic acid, and noting the odor of  $SO_2$  on heating in a flame. Rosin, vaseline, oils, etc., appear as a greasy scum on the surface of the nitroglycerin or adhering to the walls of the beaker. These substances, like sulphur, are practically insoluble in acetic acid (70%), and

may be separated from the nitroglycerin by means of this solvent. Trinitrotoluene will appear in the nitroglycerin as long yellowish needles, which may be removed, recrystallized from alcohol, and identified by their melting point (approx. 80° C.), or by the red color produced when the alcoholic solution is treated with a little caustic soda solution.

The residue insoluble in ether is replaced in the test tube and treated with water in a similar manner until all water-soluble material has been dissolved. The water solution is tested for sodium, potassium, barium, zinc, etc., and for nitrates, chlorides, etc., using the general methods of qualitative analysis.

The residue is again treated with cold dilute HCl, any effervescence being noted as indicating the presence of a carbonate, and the resulting solution tested for calcium, magnesium, zinc, etc., which may have been present as carbonates or oxides for the purpose of serving as antacids.

The residue insoluble in ether, water, and cold acid may contain wood pulp, starchy cereal products, sawdust, nitrocellulose, ground vegetable ivory (button waste), kieselguhr, ground nut shells, etc. It is most conveniently examined by means of a low-power microscope, whereby its constituents are usually readily determined. Starch is easily detected by heating a portion to boiling with dilute acid, cooling and adding a few drops of iodine solution (in KI), a blue coloration indicating starch.

**Moisture.** Moisture is best determined by desiccation over sulphuric acid, a sample of about 2 grams being spread evenly over the surface of a 3-inch watch glass and desiccated for 3 days. Continued desiccation causes a gradual loss of nitroglycerin, but the 3-day loss may be safely assumed to closely represent the actual moisture content. The time of the determination may be greatly shortened by the use of a vacuum desiccator, in which case 24 hours desiccation will give a close approximation to the true moisture content.

It must be remembered that in determining moisture in the presence of nitroglycerin, some volatilization of the latter is unavoidable, and that therefore the method followed must be an empirical one. An attempt to desiccate the sample to constant weight will show that there is undoubtedly a continual loss of nitroglycerin. This has been demonstrated<sup>1</sup> by a series of weighings of a sample exposed for a period of 459 days at a constant temperature of 33°–35° C. in an empty desiccator containing no desiccating agent. A gradual loss resulted during the entire period, totaling 17.52% of the original weight of the sample, the original moisture content of which was about 1%.

**Extraction with Ether.** Ether removes from dynamite not only the nitroglycerin, but, as has already been mentioned, sulphur, resins (present as a component or as a constituent of the wood pulp), oils (usually from cereal products present), etc. Nitrotoluenes, paraffin, vaseline, etc., are not normal constituents of straight dynamite and are considered under the type of explosive in which they are most likely to occur.

**Reflux Condenser Method.** From 6 to 10 grams of the sample is weighed in either a porcelain Gooch crucible with asbestos mat or a porous alundum filtering crucible of about 25 cc. capacity. The asbestos mat is best prepared as follows: A mixture of 1 liter of water and 5 grams of previously ignited and shredded short fibre asbestos free from hard lumps and very fine material is well shaken and about 10 cc. poured into the crucible. Suction is applied

<sup>1</sup>Storm, C. G., "The Analysis of Permissible Explosives," Bulletin No. 96, Bureau of Mines, pages 21–24, 1916.



and a smooth and perfect mat almost invariably results. The crucibles thus prepared are dried at 100° and are ready for use.

The sample in the extraction crucible is extracted with about 35 cc. of ether (U. S. P.) preferably in a continuous extraction apparatus (Wiley or similar type preferred), for about 45 minutes to 1 hour, water being continuously circulated through the condenser and the extraction tube heated on a water bath, or electric heater, the temperature of which is so regulated that the sample in the crucible will be kept covered with ether without overflowing.

**Suction Method.** If desired, the ether extraction may be carried out by suction, the Gooch crucible being held in a carbon tube passing through the stopper in a suction flask. About 100 cc. of ether in 6 to 8 portions is passed through the crucible, each portion being allowed to stand in the crucible for one minute before applying gentle suction. No more air than is necessary should be drawn through the sample in order to avoid condensation of moisture in the sample, which might dissolve a portion of the water-soluble salts. This method uses considerably more ether than the reflux condenser method and its chief advantage is that the apparatus required is more simple.

On completion of the extraction the crucible is at once placed in a drying oven, or the excess ether may be removed by suction before drying. If ammonium nitrate is present the drying should be conducted at 70° C. for 18 hours or overnight, but otherwise 5 hours at 100° C. is ample. The loss of weight represents all ether-soluble material plus the moisture in the original sample.

**Evaporation of Ether Extract.** The ether extract is washed out of the extraction tube or suction flask with a little ether into a tared evaporating dish or small beaker and the ether allowed to evaporate spontaneously in a warm place, or evaporated by means of the "bell jar evaporator."<sup>1</sup> The latter consists of a tubulated bell jar with openings at top and side, placed on a ground glass plate, a slow current of dry compressed air from two drying cylinders containing  $H_2SO_4$  and soda lime respectively, entering the top opening through a glass tube, the lower end of which extends to about one half inch from the surface of the ether solution in the beaker, which is placed on the glass plate. The dry air current striking the surface of the solution with just enough force to cause a slight "dimple," causes rapid evaporation of the ether, and deposition of moisture in the beaker along with the evaporated residue is avoided. The low temperature produced by the rapid evaporation minimizes the loss of nitroglycerin by volatilization. From 5 to 6 hours is usually required for complete evaporation, which should be determined by check weighings. If the bell jar method is not used, the residue, after removal of the ether, must be desiccated over  $H_2SO_4$  for at least 24 hours in order to remove moisture deposited during evaporation.

**Nitroglycerin.** Nitroglycerin is determined in the dried and weighed ether extract from which all ether has been removed as above described. This determination is best made by means of the du Pont modification of the 5-part Lunge nitrometer (see p. 354, Vol. I). The sample is dissolved in 5-10 cc. of pure sulphuric acid (specific gravity 1.84) and transferred to the generating bulb of the nitrometer, the beaker and cup of the nitrometer being washed with several further additions of acid until a total of 20-25 cc. has been used.

<sup>1</sup> Storm, C. G., "The Analysis of Permissible Explosives," Bulletin, 96, Bureau of Mines, page 35, 1916.

If the quantity of nitroglycerin present is too great, the sample, dissolved in sulphuric acid, is transferred to a burette and an aliquot part run into the nitrometer. The maximum amount of pure nitroglycerin used for the determination should not exceed 0.75 gram. The determination is carried out in the usual manner and the reading of the gas volume in the graduated reading tube divided by .1850 to find the weight of nitroglycerin in the sample used for the determination (pure nitroglycerin contains 18.50% N).

**Sulphur, Resins, Oils, etc.** It is always preferable to carry out the extraction with ether on duplicate samples, using one sample of the extract for the determination of nitroglycerin as above, and the other for determining sulphur, resins, oils, etc., that may also be contained in the ether extract.

The weighed extract is redissolved in a mixture of ether and alcohol, previously neutralized with standard alkali. The solution thus obtained is titrated with standard alcoholic potash solution using phenolphthalein indicator. 1 cc. of tenth normal alkali is equal to 0.034 grams of rosin (colophony).

A large excess of the alcoholic potash is now added and the mixture heated several hours or overnight on the steam bath to saponify the nitroglycerin. Shake with water and ether in a separatory funnel. The ether solution contains paraffin, vaseline, or mineral oils that may be present, and is evaporated and the residue weighed. The water solution is acidified with HCl, and Br added to oxidize any sulphur. Any separated rosin is filtered off and weighed as a check on the titration, and sulphur determined in the filtrate by precipitation as  $\text{BaSO}_4$ .

Sulphur may also be separated from nitroglycerin by means of acetic acid of approximately 70% strength, the nitroglycerin being quite soluble in acetic acid and the sulphur almost insoluble. The sulphur is filtered from the solution, washed slightly with alcohol to remove the acetic acid solution, dried and weighed.

If a considerable quantity of crystals of sulphur is found in the evaporated ether extract, it is possible that all of the sulphur has not been removed by the ether, and in this case an extraction is made with carbon disulphide, in exactly the same manner as the ether extraction. This extraction is made subsequent to the extraction with water, the sulphur being determined by loss of weight of the residue or by direct weight after evaporation of the carbon disulphide away from free flame.

**Extraction with Water and Determination of Nitrates.** The dried and weighed residue left in the crucible after extraction with ether, is extracted with water, using a suction flask fitted with a carbon filter tube in which the crucible is held by a short length of thin-walled rubber tubing. Cold water is used for this extraction, as hot water would gelatinize any starch present. A total of at least 200 cc. of water is passed through the sample, in at least 10 portions, each portion being allowed to stand in contact with the residue for a few minutes before being sucked into the flask. An evaporation test of a few drops of the filtrate will determine the completeness of the extraction. When the extraction is complete, the crucible with its insoluble residue is dried for 5 hours, or overnight, at  $95^{\circ}$ – $100^{\circ}$  C., and the loss of weight noted as total water-soluble material. This includes nitrates and other soluble salts that may be present, together with water extract from the wood pulp, flour or other absorbent. This soluble organic material may amount to as much as 2% of the total sample, when cereal products are present. Calcium, magnesium,

or zinc may also be present in solution, resulting from the action of acid decomposition products of the nitroglycerin on the carbonate or other antacid present. In routine analyses of ordinary dynamite, the loss of weight on extraction with water is usually considered as the alkaline nitrate (sodium or potassium), but where more exact results are desired an aliquot portion of the extract is evaporated to dryness with a little nitric acid to oxidize organic materials, and the residue weighed as alkaline nitrate. This weight may be corrected for inorganic impurities—chlorides, sulphates, iron, aluminum, calcium, etc.—determined separately by the usual methods.

Nitrates may be determined by means of the nitrometer, using an aliquot portion of water extract estimated to contain .6 to .8 gram of  $\text{NaNO}_3$  or .8 to 1.0 gram of  $\text{KNO}_3$ . This is evaporated on the steam bath almost to dryness and transferred with as little water as possible, to the cup of the nitrometer. This solution is drawn into the generator and 30 to 40 cc. of 95–96%  $\text{H}_2\text{SO}_4$  added slowly so as to avoid generating sufficient heat to crack the glass. The generator is then shaken for a total time of 8–10 minutes in order to be certain that the generation of gas is complete with the diluted acid. The gas is measured and the % of nitrate calculated as in the case of nitroglycerin.

**Extraction with Acid.** When starch is not present in the residue, a simple extraction of the residue insoluble in water is made with cold dilute  $\text{HCl}$  (1 : 10), 100 cc. being drawn through the sample in the crucible in small successive portions as described under "Extraction with Water." Several portions of water are then drawn through to wash out the acid, and the residue in the crucible dried for 5 hours at  $95^\circ$  to  $100^\circ \text{C}$ . The loss of weight is usually reported as antacid, but the base dissolved may be determined by the usual quantitative methods if desired. The acid-soluble materials generally present are calcium or magnesium carbonate or zinc oxide.

**Determination of Starch.** If starch is present in the residue insoluble in water, it is removed together with the antacid by boiling with dilute acid. The residue is moistened with water, scraped or washed out of the crucible into a 500 cc. beaker, the volume brought to about 250 cc. by the addition of water and 3 cc. of strong  $\text{HCl}$ , and the mixture boiled until a drop of the solution fails to give a blue color when treated on a spot plate with a drop of a solution of iodine in  $\text{KI}$ . This indicates that the starch has been completely hydrolyzed to dextrin. The mixture is then filtered through a fresh crucible, washed with water, dried and weighed, correction being made for the weight of the asbestos mat of the original crucible.

The antacid dissolved in the acid filtrate is determined as already described. The loss of weight by the boiling treatment, minus the antacid found, represents starch and other dissolved organic materials removed from cereal products or wood pulp. The insoluble residue includes the wood pulp and the crude fibre of the cereal products.

Because of the impracticability of exact separations it is customary to report all of the soluble organic material included in both water and acid extractions as "starch" or "starchy material," and the insoluble organic residue as "wood pulp and crude fibre," or the sum of these organic materials is often reported as "carbonaceous combustible material."

**Insoluble Residue and Ash.** The insoluble residue may contain wood pulp or sawdust, the crude fibre from various cereal products such as corn meal, wheat flour, middlings, bran, etc., ground nut shells, vegetable ivory meal.

and more rarely inorganic material such as infusorial earth (kieselguhr), clay, etc. These can usually be identified by microscopic examination (see Bureau of Mines Bulletin 96, Page 74), and a determination of the ash will show whether inorganic materials are present. A high ash content may also indicate incomplete water or acid extractions.

### Ammonia Dynamite

So-called ammonia dynamite is essentially "straight" dynamite in which a large part of the nitroglycerin is replaced by ammonium nitrate. The ammonium nitrate is frequently protected from moisture by a coating of vaseline or paraffin and is usually neutralized with zinc oxide. This type of dynamite generally contains less wood pulp than the corresponding grades of "straight" dynamite, and sulphur and cereal products, such as low grade flour, are usually present.

The determination of moisture and the various extractions are carried out as described for "straight" dynamite. An extraction with carbon disulphide is usually necessary to effect complete removal of the sulphur; this properly follows the extraction with water. The analysis of the ether extract may be conducted as already described. In drying the residue left in the crucible after extraction with ether, it is important that a temperature of approximately 70° C. be used, because in the presence of ZnO, the loss of ammonium nitrate is considerable at 100° C. Pure ammonium nitrate is not appreciably affected by even 24 hours heating at 100° C., but the presence of the ZnO causes decomposition at this temperature.

The water extract contains sodium nitrate and ammonium nitrate together with practically all of the zinc oxide present, the latter ingredient being dissolved with the ammonium nitrate, and a small amount of soluble organic material from the flour or other absorbent. It is analyzed as follows: An aliquot portion is evaporated to dryness in a platinum or silica dish on a steam bath, the ammonium nitrate volatilized by careful heating over a burner, a little nitric acid added to re-oxidize any nitrate that may have been reduced to nitrite, and the residue again dried on the steam bath. The zinc oxide is now in the form of zinc nitrate and may be separated from the sodium nitrate by either of the following methods:

1. The residue is dried at 110°–120° C. and weighed as  $\text{NaNO}_3$  and  $\text{Zn}(\text{NO}_3)_2$ . It is then dissolved in water, the zinc precipitated with  $\text{Na}_2\text{CO}_3$ , filtered, ignited and weighed as ZnO, and the  $\text{NaNO}_3$  taken by difference; the total  $\text{NaNO}_3$  plus  $\text{Zn}(\text{NO}_3)_2$  minus  $(\text{ZnO} \times 2.33) = \text{NaNO}_3$ .

2. The residue is gently heated over a burner until evolution of oxides of nitrogen from decomposition of the  $\text{Zn}(\text{NO}_3)_2$  has ceased, and the remaining residue weighed as  $\text{NaNO}_3$  and ZnO. It is then treated with water, the insoluble ZnO filtered on a Gooch crucible, ignited and weighed, the  $\text{NaNO}_3$  being taken by difference.

Ammonium nitrate is determined in a separate portion of the water extract by the usual method of distillation and titration.

The sum of the amounts of  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ , and ZnO found will be somewhat less than the total water extract owing to the presence of water-soluble organic material from the carbonaceous absorbents.

### Gelatin Dynamite

This is a form of nitroglycerin explosive in which the nitroglycerin, instead of being absorbed in porous materials such as wood pulp, is combined with nitrocellulose in the form of a gelatinous plastic mass. As little as 3.5% of suitable grade of nitrocellulose containing about 12% nitrogen will, when heated with nitroglycerin, at about 60° C., form a jelly-like non-fluid mass when cooled to ordinary temperature. "Blasting gelatin," used to a considerable extent where great strength is required, is a stiff colloid composed of 90 to 93% nitroglycerin and 10 to 7% nitrocellulose.

All blasting explosives containing such colloids of nitroglycerin and nitrocellulose combined with an active "dope" or base, consisting of a nitrate and combustible material, are termed gelatin dynamites. This type of explosive is also known in some countries as "Gelignite."

**Sampling.** Owing to its pasty consistency the sample of gelatin dynamite must be prepared by cutting portions of a number of cartridges into thin bits with an aluminium or platinum spatula. The use of a steel spatula or knife for this purpose is not to be recommended for reasons of safety. An ample quantity of sample thus prepared is well mixed and bottled. Owing to its tendency to again form a solid mass upon standing, it should be analyzed as soon as possible after being prepared.

**Analysis.** The principal ingredients that may be found in the different types of gelatin dynamite are nitroglycerin; nitrocellulose; sulphur; rosin; sodium, potassium or ammonium nitrate; calcium or magnesium carbonate; wood pulp, cereal products and similar carbonaceous combustible materials. Low-freezing gelatins may also contain nitrotoluenes or other nitrosubstitution compounds.

Moisture is determined as described for "straight" dynamite, and the extraction with ether made in the usual manner except that ether free from alcohol (distilled over sodium) is used in order to prevent partial solution of the nitrocellulose. The latter is readily soluble in a mixture of ether and alcohol, and as ordinary U. S. P. ether contains about 4% of alcohol, there is a possibility that an appreciable part of the 0.5% to 2.0% of nitrocellulose present in the sample will be dissolved unless pure ether is used. The ether extract is evaporated and analyzed as already described and the water extraction made in the usual manner. If more than 1 or 2% of sulphur was present it will not have been completely removed by the ether, unless the extraction was continued for a sufficiently long time. In this event, it is necessary to make an additional extraction with carbon disulphide in the Wiley apparatus subsequent to extraction with water.

**Nitrocellulose.** After the extractions with ether, water, and CS<sub>2</sub> (if necessary) have been made, the nitrocellulose is determined, preferably by extraction with acetone, which is a better solvent for the purpose than a mixture of ether and alcohol. It is advisable to separate the dry residue from the crucible, leaving the asbestos mat intact if possible. The residue is transferred to a small beaker, covered with acetone and allowed to stand at least 3 or 4 hours with occasional stirring. It is then filtered through the original crucible, washed with acetone, dried and weighed, the loss of weight being regarded as nitrocellulose. To correct for small amounts of extract from the wood pulp or other carbonaceous material, the acetone solution may be evaporated to

about 20-25 cc., and diluted gradually with a large volume (about 100 cc.) of hot water, which volatilizes the acetone, precipitating the nitrocellulose as a white flocculent mass, which is filtered, dried, and weighed.

The remainder of the analysis is conducted as for straight dynamite.

It will be found that the results of analysis of a gelatin dynamite do not agree with its trade markings. For example, the usual "40% strength" gelatin dynamite actually contains from 30 to 33% of nitroglycerin and about 1% of nitrocellulose. Weight for weight this explosive is considerably weaker than 40% straight dynamite, which contains 40% of nitroglycerin.

### Low-Freezing Dynamite

Low-freezing dynamites vary from the dynamite types already discussed by containing an ingredient which reduces the freezing point of the nitroglycerin. This ingredient replaces a portion of the nitroglycerin which would be used in an equal grade of ordinary straight dynamite, ammonia dynamite, or gelatin dynamite. While straight nitroglycerin dynamite may freeze at temperatures as high as 8° C. (46° F.), some of the low-freezing dynamites freeze only at temperatures considerably below 0° C. Many of this type, however, cannot be relied upon to resist freezing at temperatures below the freezing point of water.

The additions made to nitroglycerin for this purpose include the nitrotoluenes, nitroxylenes, nitrohydrins, nitrosugar, and nitropolyglycerin (tetranitrodiglycerin). Any of these substances present will be found in the ether extract together with, and in most cases dissolved in, the nitroglycerin.

**Moisture.** The determination of moisture is carried out as already described for "straight" nitroglycerin dynamite (p. 1375). Attention has been called to the fact that certain nitrosubstitution compounds, notably the mono- and dinitrotoluenes, are more or less volatile and would therefore be partly lost if the moisture is determined in a vacuum desiccator. The safest procedure is therefore to determine the moisture by desiccation for 3 days without vacuum. The difference between the total loss on extraction with ether and the direct weight of the ether extract, after evaporation of the ether in a bell-jar evaporator (p. 1376), should be equal to the moisture content of the sample. This figure will therefore serve as a check on the result obtained by desiccation.

**Nitrotoluenes.** Trinitrotoluene is not readily soluble in nitroglycerin and separates as crystals on evaporation of the ether from the ether extract, enabling it to be qualitatively separated and identified. It may be determined by difference, the nitroglycerin being determined by means of the nitrometer. Any dinitrotoluene present may also be determined in this manner together with the trinitrotoluene, but if mononitrotoluene is also present, the determination of the nitrogen of the nitroglycerin will be slightly in error by about 0.5530 gram of nitroglycerin for every gram of mononitrotoluene present.<sup>1</sup>

Mononitrotoluene is, however, seldom present except as an impurity in the so-called liquid di- and trinitrotoluenes used in low freezing dynamites, so that the determination of the nitroglycerin is usually fairly accurate and the nitrotoluenes may be calculated by difference.

<sup>1</sup> Storm, C. G., "The Effect of Nitrotoluenes on the Determination of Nitroglycerin by Means of the Nitrometer," *Proc. 8th Int. Cong. Appl. Chem.*, Vol. 4, 1912, p. 117; also *Bu. of Mines Bull.* 41, p. 62, 1913.

The total nitrogen of the combined nitroglycerin and nitrosubstitution compound may also be determined, the nitrogen of the nitroglycerin deducted and the amount of nitrosubstitution compound calculated from the resulting difference, if the identity of the nitrosubstitution compound has been established. A suitable modification of the Kjeldahl method which has been found applicable to difficultly decomposable nitrocompounds is as follows:<sup>1</sup> This method is, of course, applicable to mixtures containing nitroglycerin.

**Modified Kjeldahl Method for Nitrogen.** About 0.5000 g. of the nitrocompound is weighed into a 500 cc. Kjeldahl flask, 30 cc. of 96%  $\text{H}_2\text{SO}_4$  and 2 g. salicylic acid added and the sample dissolved by heating on a steam bath if necessary. Cool; add 2 g. zinc dust in small portions, with cooling and rotating the flask. Continue the shaking at 15 minute intervals for 2 hours and let stand overnight. Then heat over a small flame till fuming has ceased (about 2 hours), cool slightly and add 1 g.  $\text{HgO}$  and boil  $1\frac{1}{2}$  hours longer. Cool and add 7.5 g.  $\text{K}_2\text{SO}_4$  and 10 cc.  $\text{H}_2\text{SO}_4$  and boil  $1\frac{1}{2}$  to 2 hours more. If the solution is not clear and almost colorless, add 1 g. more  $\text{K}_2\text{SO}_4$  and boil longer. Cool and add 250 cc.  $\text{H}_2\text{O}$  to dissolve the cake formed, then add 25 cc.  $\text{K}_2\text{S}$  solution (80 g. per liter  $\text{H}_2\text{O}$ ), 1 g. granulated  $\text{Zn}$ , and 85–90 cc.  $\text{NaOH}$  solution (750 g. per liter  $\text{H}_2\text{O}$ ), and distill as usual in the Kjeldahl determination, collecting the  $\text{NH}_3$  in standard  $\text{H}_2\text{SO}_4$  solution. A blank determination without sample is advisable.

**Separation of Nitrocompounds from Nitroglycerin.** Hyde has devised a satisfactory method for actual separation of nitrosubstitution compounds from nitroglycerin, depending on the differences in solubility of these ingredients in carbon bisulphide and dilute acetic acid.<sup>2</sup> Nitroglycerin is only slightly soluble in  $\text{CS}_2$ , but readily soluble in dilute acetic acid, while most nitrocompounds are much more soluble in  $\text{CS}_2$  and much less soluble in dilute acetic acid than nitroglycerin.  $\text{CS}_2$  and acetic acid are only slightly miscible. Hence nitroglycerin and a nitrocompound may be partly separated by shaking the mixture with  $\text{CS}_2$  and dilute acetic acid, allowing the two solvents to separate into two layers and drawing off one of the layers. The  $\text{CS}_2$  layer will contain most of the nitrocompound and the acetic acid layer most of the nitroglycerin.

Hyde's method involves a continuous fractional extraction in a rather complicated apparatus consisting of 13 long narrow extraction tubes, connected with each other and with a condenser, reservoir and distilling flask so as to form a closed circulating system, the  $\text{CS}_2$  continually passing in a train of fine drops through acetic acid in the series of extraction tubes, carrying with it the nitrocompound, the nitroglycerin tending to remain dissolved in the acetic acid. Practically a complete separation is finally obtained, the nitrocompound dissolved in the  $\text{CS}_2$  collecting in the distilling flask at the end of the extraction train and the nitroglycerin remaining in solution in the acetic acid in the tubes. The  $\text{CS}_2$  is evaporated and the nitrocompound weighed. Reference should be made to the original article by Hyde for details as to construction and operation of the apparatus.

<sup>1</sup> Cope, W. C., "Kjeldahl Modification for Determination of Nitrogen in Nitrosubstitution Compounds," *J. Ind. and Eng. Chem.*, Vol. 8, p. 592, 1916.

<sup>2</sup> Hyde, A. L., "The Quantitative Separation of Nitrosubstitution Compounds from Nitroglycerin," *J. Am. Chem. Soc.*, Vol. 35, p. 1173, 1913. (See also *Bu. Mines Bulletin*, 96, pp. 47–50, 1916.)



**Nitrosugars.** The nitrates of sugar, improperly called nitrosugar, are used to a considerable extent for lowering the freezing point of nitroglycerin. This substance is soluble in nitroglycerin, being prepared with the latter by nitrating a solution of cane-sugar in glycerin, and no method is known for its separation from nitroglycerin. Hoffman and Hawse<sup>1</sup> have reported on an optical method for the determination of nitrated sugar in nitroglycerin mixtures, based on the use of the polariscope. As an example of the application of the method, 10.65 g. of a nitrated mixture of glycerin and sugar was dissolved in 100 cc. alcohol and its angle of rotation found to be  $\alpha = 3.07^\circ$ . The specific rotatory power of sucrose octanitate having been determined as  $\alpha = 56.66$ , the formula:  $C \text{ (concentration)} = \alpha / 2\alpha$  gives a result of 25.44% sucrose octanitate in the sample.

The result of the optical method may be roughly checked by a determination of the total nitrogen of the combined nitroglycerin and nitrosugar, assuming the nitrogen content of the nitrosugar to be 15% (theoretical for sucrose octanitate 15.95%), and that of nitroglycerin 18.50%.

**Nitrochlorhydrins.** Dinitromonochlorhydrin has been known for years as a partial substitute for nitroglycerin in explosives. It is a solvent for nitrocellulose in smokeless powders and has an appreciable effect in lowering the freezing point of nitroglycerin. During recent years it has come into use in this country as a substitute for nitrotoluenes in low freezing dynamites.

A mixture of dinitrochlorhydrin and nitroglycerin will have a lower nitrogen content than pure nitroglycerin, the dinitrochlorhydrin containing only 14.0% N, as compared with 18.50% N in nitroglycerin. The dinitrochlorhydrin may be readily identified and determined quantitatively by treating the mixture containing this substance and nitroglycerin with an excess of alcoholic solution of KOH, heating on the steam bath until saponification is complete, and determining the chlorine in the solution as chloride.

It must be noted that dinitrochlorhydrin is somewhat more volatile than nitroglycerin and therefore in evaporating the ether from the ether extract it is advisable to make use of the bell-jar evaporator (p. 1376) so as to minimize its loss during evaporation.

**Nitropolyglycerin.** Nitrated polymerized glycerin—usually a mixture of tetranitrodiglycerin and trinitroglycerin—is sometimes found in low-freezing explosives. This mixture will show a lower N-content than nitroglycerin, since pure tetranitrodiglycerin contains only 16.19% N. The presence of the latter substance is indicated by low solubility in dilute acetic acid (60 volumes glacial acetic acid to 40 volumes water). One gram of nitroglycerin dissolves in about 10.5 cc. of this acid, while 1 gram of a mixture containing 82.25% tetranitrodiglycerin required 120 cc. of the acetic acid to completely dissolve it. In dissolving such a mixture, it will be found that a part of the mixture dissolves more readily than the remainder. If the more difficultly soluble portion is separated, dried in a desiccator and its nitrogen content determined in the nitrometer, it will be found to contain a much lower % N than the original mixture, approximating the figure for tetranitrodiglycerin, 16.19% (an actual trial gave 16.24% N).

If the presence of tetranitrodiglycerin is established by the above procedure and no other substances except nitroglycerin are present, the proportions of these two ingredients in the ether extract may be readily calculated from the N-content as found by the nitrometer.

<sup>1</sup> Hoffman, E. J. and Hawse, V. P., "The Nitration of Sucrose Octanitate," J. Am. Chem. Soc., Vol. 41, pp. 235-247, 1919.



**"PERMISSIBLE" EXPLOSIVES**

"Permissible" explosives are coal mining explosives which have passed the prescribed tests of the Bureau of Mines and are recommended by the Bureau for use in gassy and dusty mines. Their important characteristic is a relatively low flame temperature, which is brought about by modifying the composition of the usual types of dynamites and other blasting explosives. The general methods of reducing the flame temperature of explosives<sup>1</sup> are summarized as follows:

- (a) Addition of an excess of carbon,—forming less CO<sub>2</sub> and more CO in the gases of explosion.
- (b) Addition of free water or of solids with water of crystallization.
- (c) Addition of inert materials.
- (d) Addition of volatile salts.

The analysis of explosives of this class is therefore generally more complicated than that of the ordinary types of blasting explosives because of the greater variety of ingredients used in manufacture. A partial list of substances which have been found in low-flame explosives manufactured in this country is shown below, arranged according to their solubility in the general scheme of analysis:

<i>Soluble in Ether</i>	<i>Soluble in Water</i>	<i>Soluble in Acids</i>
Nitroglycerin	Ammonium nitrate	Aluminum
Nitropolyglycerin	" chloride	Calcium carbonate
Nitrotoluenes	" sulphate	" silicide
Nitrosugars	" oxalate	Ferric oxide
Nitrochlorhydrins	" perchlorate	Magnesium carbonate
Paraffin	Alum (cryst.)	Zinc
Resins	Aluminum sulphate (cryst.)	Zinc oxide
Sulphur	Barium nitrate	
Vaseline	Calcium sulphate (cryst.)	
Oils	Gums	
	Magnesium sulphate (cryst.)	
	Potassium chlorate	
	" nitrate	
	" perchlorate	
	Sodium nitrate	
	" chloride	
	" bicarbonate	
	" carbonate	
	Sugar	
	Zinc oxide	
	<i>Insoluble</i>	
	Charcoal	Peanut shell meal
	Clay	Powdered slate
	Coal	Rice hulls
	Corn meal	Sawdust
	Corn cob meal	Turmeric
	Kieselguhr	Vegetable ivory meal
	Nitrocellulose	Wheat flour
	Nitrostarch	Wood pulp
	Nitrated wood	

<sup>1</sup> The thermochemical considerations involved are discussed in Bureau of Mines Bulletin No. 15, "Investigations of Explosives used in Coal Mines," 1912, and details of analysis in Bureau of Mines Bulletin No. 96, "The Analysis of Permissible Explosives," C. G. Storm, 1916.

**Qualitative Analysis.** The qualitative examination of a "permissible" explosive is conducted in the same manner as has been described for dynamite (see page 1374), and, in view of the greater variety of constituents that may be present, is quite essential before a suitable scheme for quantitative separation can be chosen.

Tests for some of the more unusual substances not generally found in the ordinary types of blasting explosives, and not already discussed under "Low-freezing Explosives," are made as follows:

**Test for Sugar.** The presence of water-soluble organic substances is indicated by an appreciable charring of the residue obtained by evaporating a portion of the water extract to dryness and then heating gradually over a burner. A slight charring may result from water-soluble portions of cereal products, wood-pulp, etc., and may be disregarded. Sugar is identified by acidifying some of the water solution with a little dilute HCl, heating to boiling, neutralizing with KOH and then boiling with Fehling's solution. A precipitation of cuprous oxide indicates the presence of sugar.

**Test for Gum Arabic.** Gum arabic is precipitated by the addition of a solution of basic lead acetate to the water extract, a white, flocculent precipitate of indefinite composition resulting (see Determination of Gum Arabic, p. 1388).

**Test for Nitrostarch.** Nitrostarch is best identified by microscopic examination of the residue insoluble in water. It is easily distinguished from unnitrate starch by means of a solution of iodine in KI, which colors the starch granules dark blue but does not affect the granules of nitrostarch.

**Test for Chlorides, Chlorates, and Perchlorates.** These three substances present in a solution may be identified as follows: Acidify slightly with nitric acid, add excess of  $\text{AgNO}_3$ , heat to boiling, shake well, and filter off the silver chloride. To the filtrate add a few cc. of 40% solution of formaldehyde (formalin), and boil to reduce chlorates to chlorides. This reduction is best carried out by heating on the steam bath for about an hour. Any chloride thus formed is then separated by further precipitation with  $\text{AgNO}_3$  and removed by filtration. The filtrate is then evaporated to dryness, the residue transferred to a crucible and fused with dry  $\text{Na}_2\text{CO}_3$ . The fused mass is treated with dilute  $\text{HNO}_3$ , when the presence of perchlorate will be indicated by an insoluble precipitate of  $\text{AgCl}$ .

**Mechanical Separation of Solid Ingredients.** It is frequently of advantage, especially in connection with the interpretation of the results of analysis of an explosive mixture containing a number of water-soluble salts, to determine the identity of one or more of the components of the mixture by means of screening or by a method of separation depending on variation in specific gravity of the components. Such methods are facilitated by the fact that the ingredients of blasting explosives are frequently not finely pulverized in the course of manufacture.

(a) *By Screening.* 25 to 50 grams of the sample is washed several times with ether to remove nitroglycerin and ingredients of an oily nature, the solid residue dried to remove adhering ether and then sifted through a set of sieves. An examination of the portions held by the 10- and 20-mesh screens will usually show the presence of coarse crystals which are large enough to be sorted out with the aid of forceps, submitted to qualitative tests and identified with certainty. A single crystal may sometimes be identified by dissolving it in a drop of water on a microscope slide, allowing the water to evaporate and

examining the resulting crystals under the microscope. The writer has frequently identified three or four ingredients of an explosive in this manner.

(b) *By Specific Gravity Separations.* This method, applied to the analysis of explosives by Storm and Hyde,<sup>1</sup> depends on the separation of solids from a mixture by means of inert liquids of different specific gravities. A series of mixtures of chloroform (sp.gr. 1.49) and bromoform (sp.gr. 2.83) is prepared covering as wide a range of specific gravity as may seem desirable. Portions of the dried sample previously extracted with ether as in (a) are added to such liquid mixtures and the heavier salts, which settle to the bottom, separated from the lighter ones. For example a mixture of ammonium nitrate (sp.gr. 1.74) and sodium chloride (sp.gr. 2.17) is readily separated into its components in a liquid with a specific gravity of (*e.g.*), 1.90, so that the components can be tested separately and the analyst assured that the mixture is not composed of sodium nitrate and ammonium chloride,—which could not be ascertained by ordinary quantitative analysis. (For example, a mixture composed of 16.61% Na, 44.76% NO<sub>3</sub>, 13.00% NH<sub>4</sub> and 25.63% Cl may contain either 61.37% NaNO<sub>3</sub> and 38.63% NH<sub>4</sub>Cl, or 57.76% NH<sub>4</sub>NO<sub>3</sub> and 42.24% NaCl, or varying proportions of all four ingredients.) The chloroform-bromoform mixtures are recovered by filtering and used repeatedly.

The specific gravities of some of the more common salts that may be found are as follows:

Ammonium alum (cryst.)	1.62
“ chloride	1.52
“ nitrate	1.74
“ perchlorate	1.87
“ sulphate	1.77
Barium nitrate	3.23
Calcium carbonate (ppt'd)	2.72
“ sulphate (anhydrous)	2.97
“ sulphate + 2H <sub>2</sub> O	2.32
Magnesium carbonate	3.04
“ sulphate + 7H <sub>2</sub> O	1.68
Manganese dioxide	5.03
Potassium alum (cryst.)	1.75
“ chlorate	2.33
“ chloride	1.99
“ nitrate	2.09
“ perchlorate	2.52
“ sulphate	2.66
Sodium chloride	2.17
“ nitrate	2.26
“ sulphate (anhydrous)	2.66
“ sulphate + 10H <sub>2</sub> O	1.46

**Moisture.** The determination of moisture in all types of “permissible” explosives is carried out by the method described for nitroglycerin dynamites (page 1375). The influence of the slight volatility of nitroglycerin and of certain nitrosubstitution compounds on the results of this determination has been discussed (pp. 1375, 1381). A more serious factor in the case of many “permissible” explosives is the presence of salts containing water of crystallization. Most salts of this type (*e.g.*, MgSO<sub>4</sub>·7H<sub>2</sub>O) undergo a gradual loss of a large part of their combined water on desiccation over either H<sub>2</sub>SO<sub>4</sub> or CaCl<sub>2</sub>, thus rendering it impossible to differentiate between hygroscopic moisture and

<sup>1</sup> Storm, C. G., and Hyde, A. L., “Specific Gravity Separation Applied to the Analysis of Mining Explosives,” Tech. Paper No. 78, Bureau of Mines, 1914.

combined water. Attempts to remove the total water content by heating at a temperature high enough to drive off all of the water of crystallization are useless on account of the increased volatilization of nitroglycerin, ammonium nitrate, etc., at such temperatures.

In such cases it is necessary to determine all other constituents by direct methods and estimate moisture by difference, the salt to which the water of crystallization belongs being calculated as containing its full quota of water; or the crystallized salt may be calculated as anhydrous and the difference from 100% reported as "water of crystallization plus moisture."

**Extraction with Ether.** The extraction with ether, the evaporation of the ether, and the analysis of the ether-soluble portion are conducted as already discussed for nitroglycerin dynamites (pp. 1375, 1376).

In drying the crucibles containing the residue insoluble in ether, a temperature of 100° C. may be used except when the residue contains ammonium nitrate or organic nitrates such as nitrocellulose, nitrostarch, or nitrated wood. When any of these substances are present, the residue should be dried to constant weight at 70° C. Except when salts containing water of crystallization are present, the amount of ether-soluble material found is calculated by deducting the moisture determined by desiccation, from the difference between the weight of original sample and the weight of the dried residue insoluble in ether. The procedure followed when water of crystallization is present is noted in the preceding paragraph.

**Extraction with Water.** Water-soluble salts are extracted from the weighed residue insoluble in ether as already described, the residue left in the crucibles dried to constant weight at 95 to 100° C., cooled and weighed. The water soluble salts in the solution are determined by the usual methods of inorganic analysis.

**Nitrates.** In determining nitrates by the nitrometer method (see p. 354) it must be remembered that the presence of a considerable quantity of chlorides may interfere with the accuracy of the results. Many of the "permissible" explosives contain sodium chloride in amounts varying from 1% to 10 or 15%. M. T. Sanders<sup>1</sup> has shown that if the sodium chloride is present in an amount exceeding 15-17% of the sodium nitrate, the result is not accurate within 0.1%. Smaller amounts of sodium chloride do not interfere, except to increase the amount of sludge formed in the nitrometer.

Nitrates may also be determined by the "nitron" method of Busch.<sup>2</sup>

**Chlorates.** Chlorates may be determined by any of the methods described on page 152 (reduction with SO<sub>2</sub>, FeSO<sub>4</sub>, or Zn) or by the formaldehyde method.<sup>3</sup> In the latter method a portion of the solution, containing about 0.5 g. of chlorate is diluted to 150 cc., 5-10 c. of 40% formaldehyde solution, 2 cc. dilute HNO<sub>3</sub> (1 : 3), and 50 cc. of approx. tenth normal silver nitrate added, the solution covered and heated on the steam bath for about 4 hours, when the precipitate of AgCl is filtered off, washed, dried and weighed. This method is accurate to .05 to .10%.

<sup>1</sup> Sanders, M. T., "The Effect of Chlorides on the Nitrometer Determination of Nitrates," *J. Ind. & Eng. Chem.*, 12, p. 169-170, 1919.

<sup>2</sup> See page 345, also, for further details, "The Analysis of Permissible Explosives," Bureau of Mines, Bulletin 96, pages 60-2.

<sup>3</sup> Storm, C. G., "The Analysis of Permissible Explosives," Bulletin 96, Bureau of Mines, pp. 63-4, 1916.

**Perchlorates.** The determination of perchlorates by reduction to chlorides on ignition with  $\text{NH}_4\text{Cl}$  in the presence of platinum is described on page 1128. Perchlorates may also be determined by means of precipitation with "nitron" in exactly the same manner as for nitrates. The weight of nitron perchlorate ( $\text{C}_{10}\text{H}_{14}\text{N}_4\text{HClO}_4$ ) found, multiplied by 117.5 (mol. wt. of  $\text{NH}_4\text{ClO}_4$ ) and divided by 412.5 (mol. wt. of nitronperchlorate) gives the weight of perchlorate found, expressed as  $\text{NH}_4\text{ClO}_4$ .

**Gum Arabic.** This substance, sometimes used as a binder in dry explosive mixtures—especially chlorate or perchlorate powders—is determined by precipitation with basic lead acetate solution, prepared by adding 150 g. of normal lead acetate and 50 g. lead oxide ( $\text{PbO}$ ) to 500 cc. distilled water, heating almost to boiling, and filtering. This reagent is added to the solution containing the gum arabic until no further precipitation occurs; the mixture is allowed to stand for several hours, then filtered, washed with absolute alcohol, dried at  $100^\circ$  and weighed. The weight of precipitate multiplied by the factor 0.4971 (determined experimentally) gives the weight of gum arabic found. Chlorides or sulphates, if present, interfere with the determination and must be first removed.

**Sugar.** Sugar may be present as an ingredient in some "permissible" explosives, and is always found in small amounts in the water extract if cereal products such as corn meal or wheat middlings are present. A portion of the water extract is acidified with  $\text{HCl}$  (1 cc. conc.  $\text{HCl}$  to 100 cc. solution), heated just to boiling, cooled, nearly neutralized with  $\text{Na}_2\text{CO}_3$ , an excess of Fehling's solution added and the mixture heated until reduction is complete. The  $\text{Cu}_2\text{O}$  is filtered from the blue liquid, dried, ignited to constant weight, and weighed as  $\text{CuO}$ . This weight  $\times 0.4308$  equals weight of cane sugar. The result is corrected for the result of a blank determination using distilled water instead of the water extract. By the use of this method after first extracting with ether, then with water, corn meal was found to contain 2.65% and wheat middlings 6.25–7.00% of sugar. Thus an explosive containing 25% wheat middlings would show as much as 1.75% of sugar in its water extract.

**Extraction with Acid.** As in the ordinary nitroglycerin dynamites, the substances removed from "permissible" explosives by acid extraction are chiefly substances added as antacids, including calcium carbonate, magnesium carbonate and zinc oxide. Other acid-soluble materials that may be present include metallic aluminum or zinc, ferric oxide, manganese dioxide, and calcium silicide. When starch is present, the residue from the water extraction is subjected to hydrolysis in boiling dilute  $\text{HCl}$  as already described (page 1378), and the acid-soluble inorganic components determined in the filtrate by the usual methods. An extraction with cold acid is made only when there is no starch present.

**Extraction with Acetone: Nitrocellulose and Nitrostarch.** If either nitrocellulose or nitrostarch is present, an extraction with acetone is made as described for gelatin dynamite (page 1401). It should be noted in connection with the preceding steps in the analysis that in order to avoid partial solution of these substances in ether, the ether used in the ether extraction should be alcohol-free (distilled from sodium), and also that all drying of residues containing these materials should preferably be conducted at  $70^\circ$  instead of  $100^\circ$ , in order to avoid partial decomposition. It is impracticable to separate nitrostarch from nitrocellulose but they are not likely to be found together in the

same explosive. Small amounts of nitrocellulose are detected less readily than nitrostarch, which is easily identified by the microscope.

**Insoluble Residue and Ash.** The insoluble residue is usually carbonaceous combustible or absorbent material and is in most cases readily identified by means of a microscope (preferably binocular) with low power (25–50 diameters). The possible presence of any inorganic material which may have been overlooked in the analysis is detected by means of a determination of ash, the residue being ignited until all carbon is burned off and the mineral residue weighed. This is usually not over 0.2%. If higher than 0.5%, there is reason to suspect that some such material as kieselguhr or clay is present, or that the extractions with water or acid were not complete.

## NITROSTARCH EXPLOSIVES

**General Nature.** Nitrostarch explosives have been for a number of years used to a very considerable extent in this country for commercial blasting purposes, chiefly for quarrying. During the war, explosives of this class were adopted by the United States for certain military purposes and proved satisfactory substitutes for trinitrotoluene as bursting charges for hand grenades, rifle grenades and trench mortar shell.

The commercial nitrostarch explosives may contain, in addition to the nitrostarch, any or all of the following components: oxidizing agents, as sodium or ammonium nitrates, combustible material, such as charcoal, flour, sulphur, etc., mineral oil, and antacids, such as calcium carbonate, or zinc oxide. Nitrostarch military explosives may consist of some such mixture as the above, or may be composed almost entirely of nitrostarch with the addition of relatively small amounts of oils and materials used for granulating. Some types of nitrostarch explosives proposed for military use contained water in amounts up to 10–15% combined with a mixture of nitrostarch and a soluble nitrate.

For commercial use, nitrostarch explosives are put up in cartridge form in paper wrappers, just as nitroglycerin explosives are prepared.

**Moisture.** Moisture is determined as in the case of nitroglycerin dynamites. 3 to 5 grams of the sample is desiccated over sulphuric acid for 2–3 days (2 days is usually sufficient to give constant weight), or for 24 hours in a vacuum desiccator with a vacuum of at least 700 mm. of mercury. Unlike nitroglycerin, nitrostarch does not volatilize and may be desiccated to constant weight. When heated to higher temperatures, *e.g.*, 100° C., for any extended time, it undergoes, like all nitric esters, a gradual decomposition with loss of weight.

**Extraction with Petroleum Ether: Oils, Sulphur, etc.** The small amount of alcohol usually present in ordinary grades of ethyl ether, is sufficient to cause partial solution of the nitrostarch, if ethyl ether is used for removing oily ingredients, sulphur, etc., nitrostarch being readily soluble in mixtures of ether and alcohol. It is therefore advisable to use petroleum ether, which does not dissolve nitrostarch, for this extraction.

A sample of about 10 grams of the explosive, in a Gooch crucible with asbestos mat, is extracted with pure petroleum ether of about 0.65 specific

gravity, the excess solvent removed by suction and the crucible with sample dried to constant weight at approximately 70° C. The % loss of weight, minus the moisture content, already determined, represents the percentage of ether-soluble material present. The petroleum ether is removed by evaporation, the residue of ether-soluble materials dried, weighed, and its components determined by the methods used for dynamites.

**Extraction with Water: Nitrates, Gums, etc.** The dried and weighed residue insoluble in petroleum ether is extracted with distilled water to remove the nitrates or other water-soluble materials. The insoluble residue left in the crucible is dried at a temperature of 80° C. (100° may cause some decomposition of the nitrostarch) for several hours, and weighed, the loss of weight being total water extract and serving as a check against the sum of the components separately determined.

Ammonium nitrate, if present, is determined in the water solution by the usual method of distillation of the  $\text{NH}_3$  after adding an excess of alkali. Sodium nitrate is determined by evaporating the water extract, volatilizing ammonium salts, and weighing the residue after re-oxidizing with nitric acid if charring has indicated the presence of any water-soluble organic material (page 1378).

If the original explosive is granular in form, the presence of a binding or agglutinating material in the water extract may be suspected. Although numerous other substances may be used for the purpose, gum arabic is frequently employed as a binding agent in different types of dry explosives. A qualitative test for gum arabic has been mentioned on page 1385, and its quantitative determination may be conducted as described on page 1388, by precipitation with basic lead acetate solution.

**Insoluble Residue: Nitrostarch, Charcoal, Cereal Products, etc.** *Starch.* A microscopic examination of the weighed insoluble residue will usually serve to identify its components. Any un-nitrated starch or cereal products is readily distinguished from nitrostarch by treating with a drop of KI solution of iodine and examining under the microscope, when the un-nitrated starch granules will appear blue or black and the nitrated starch colorless or yellow. Charcoal is identified by its color.

Un-nitrated starch, if present in an amount greater than a trace, is determined by boiling with dilute  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  until iodine solution no longer colors a drop of the liquid blue, then filtering and washing thoroughly. The residue is dried at 100° and weighed, the loss of weight representing starch.

*Nitrostarch.* Another portion of the insoluble residue (the analysis being conducted in duplicate), is extracted with acetone in a Wiley extractor or other continuous extraction apparatus, or by transferring the residue from the crucible to a small beaker, digesting in acetone with stirring, and filtering through the same crucible, washing with fresh acetone. This extraction dissolves all of the nitrostarch, leaving any charcoal or cereal products that may be present. The residue is dried at 100° and weighed, the loss of weight representing nitrostarch.

The nitrogen content of the nitrostarch may be determined, if desired, by precipitating the nitrostarch from the clear acetone solution by the addition of water and evaporation on a steam bath. A portion of the white, floury precipitate is then dried at 70°-80° C., weighed, and its nitrogen content determined in the nitrometer (see page 354 Vol. I).



**Charcoal.** If charcoal is present its weight may be taken direct, in the absence of cereal products or other substances. When the residue contains cereal products, the material left after hydrolysis of the starch and extraction of the nitrostarch will contain the crude fibre of the cereal together with charcoal or other insoluble ingredients. A separation of such components is usually impracticable.

### Trinitrotoluene (TNT.)

Trinitrotoluene, commonly designated in this country by the abbreviation TNT., is also known in this and other countries by such names as triton, trotyl, tolite, trilit, trinol, tritolo, etc. The term trinitrotoluol, which is probably more commonly used than trinitrotoluene, is incorrect according to approved chemical nomenclature.

This explosive is of the greatest importance as a high explosive for military use, being adaptable as a bursting charge for high explosive shell, trench mortar shell, drop-bombs, grenades, etc., because of its powerful explosive properties, relative safety in manufacture, handling, etc., its stability, its lack of hygroscopicity, and absence of any tendency to form sensitive compounds with metals.

It is classified by the Ordnance Department, U. S. A., into three grades, according to purity—Grades I, II, and III, with solidification points of at least 80.0°, 79.5°, and 76° C., respectively. Other requirements—the same for all grades—are as follows: ash, not more than 0.1%; moisture, not more than 0.1%; insoluble, not more than 0.15%; acidity, not more than 0.01%.

**Solidification Point.** The determination of the solidification point or "setting point" of TNT. is the best single test for purity of this compound, and is preferably carried out as follows:

A sample of about 50 grams of TNT. is placed in a 1"×6" test tube and melted by placing the tube in an oven at about 90° C. The tube is then inserted through a large cork stopper into a larger test tube about 1½"×7", which, in turn, is lowered into a wide-mouth liter bottle, so that the rim of the large tube rests on the neck of the bottle. The inner test tube is provided with a cork stopper containing 3 openings—one for a standard thermometer graduated in 1/10° C., one for a short thermometer which is passed just through the stopper and is used for noting the average temperature of the exposed mercury column of the standard thermometer, and the third opening being a small v-shaped notch at the side of the stopper, through which passes a wire whose lower end is bent in a loop at right angles to the axis of the tube and which is used for stirring the molten sample of TNT.

The standard thermometer is so adjusted that its bulb is in the center of the molten mass, and the stirrer is operated vigorously, the thermometer being watched carefully as the temperature falls. The temperature will finally remain constant for an appreciable time and then rise slightly, owing to the heat of crystallization of the TNT. As this point is reached, readings should be taken about every 15 seconds until the maximum temperature of the rise is reached. This temperature will usually remain constant for several minutes while crystallization is proceeding. The maximum reading, corrected for the emergent stem of the thermometer, is taken as the solidification point of the sample.



**Ash.** About 5 grams of TNT. is moistened with sulphuric acid and burned in a tared crucible. The residue is again moistened with a few drops of nitric acid and sulphuric acid and again ignited and the resulting ash weighed.

**Moisture.** A sample of about 5 grams spread on a watch glass is desiccated over sulphuric acid to constant weight.

**Insoluble.** A sample of about 10 grams is treated with 150 cc. of 95% alcohol, heated to boiling, and filtered while hot through a tared Gooch crucible with asbestos mat. The insoluble residue is washed with hot alcohol, dried at 100° C. and weighed.

**Acidity.** A 10-gram sample is melted in a large test tube or a flask and shaken with 100 cc. of neutralized boiling water, cooled and the water decanted. A similar treatment is given using 50 cc. of boiling water, the two portions of water combined, cooled and titrated with tenth normal NaOH, using phenolphthalein indicator. The acidity is calculated as %  $H_2SO_4$  in the original sample.

**Nitrogen.** Nitrogen is not usually determined in the inspection of TNT. but when necessary it may be determined by the Dumas combustion method or the modification of the Kjeldahl method described on page 1382.

### Picric Acid

Ordinance Department, U. S. A., specifications for picric acid prescribe that it shall have a solidification point of not less than 120° C.; that it shall contain not more than the following amounts of impurities:

Moisture—0.2% for dry material.....	12.0% for wet.
Sulphuric acid (free and combined).....	0.10%
Ash .....	0.2%
Insoluble in water.....	0.2%
Soluble lead.....	0.0004%
Nitric acid (free). ....	none

**Solidification Point.** Dry the sample at a temperature not exceeding 50° C. Melt sufficient to give a 3-inch column in a 6-inch  $\times$   $\frac{3}{4}$ -inch test tube immersed in a bath of glycerin heated to 130° C. When the sample is completely melted remove the tube from the bath and stir the sample with a standardized thermometer graduated in 0.10 degrees, until the picric acid solidifies. During solidification the temperature will remain constant for a short time and then undergo a slight rise. The highest temperature reached on this rise is recorded as the solidification point. The test may be more accurately carried out using the apparatus and method as described under trinitrotoluene (p. 1391).

**Moisture.** A weighed sample of about 10 grams is spread evenly on a tared watch glass and dried to constant weight (about 3-4 hours) at 70° C.

**Sulphuric Acid.** About 2 grams is weighed and dissolved in 50 cc. of distilled  $H_2O$ , acidified with HCl and heated to about boiling. Hot  $BaCl_2$  solution is added with stirring and the mixture allowed to stand at least 1 hour on the steam bath. Filter hot on a tared Gooch crucible, wash with water, dry at 100° C. and weigh. Calculate  $BaSO_4$  found as  $H_2SO_4$  in original sample.

**Ash.** About 1 gram is weighed in a platinum crucible, saturated with melted paraffin, burned carefully, and the residue ignited to burn off all carbon. The resulting ash is cooled and weighed.

**Insoluble in Water.** 10 grams of the sample is treated with 150 cc. boiling water, boiled for 10 minutes, filtered while hot through a tared Gooch crucible, washed well with hot water, and the insoluble residue on the filter dried at 100°, cooled, and weighed.

**Soluble Lead.** The presence of soluble lead in picric acid is highly objectionable, because lead picrate is an extremely sensitive explosive and its presence would greatly increase the dangers involved in handling and loading picric acid. A weighed sample of about 300 g. is digested in a 2-liter flask with 100 cc. of a hot saturated solution of barium hydroxide in 65% alcohol. 1400 cc. of 95% alcohol is then added and the digestion continued at a temperature below the boiling point (with reflux condenser), until everything except traces of insoluble matter is in solution. The picric acid is then allowed to crystallize on cooling, and the solution filtered off, decanting the clear liquid from the crystals until 500 cc. of filtrate is obtained. This 500 cc., representing 100 g. of picric acid, is treated with 5 drops  $\text{HNO}_3$  and 10 cc. of 1%  $\text{HgCl}_2$  solution, and  $\text{H}_2\text{S}$  passed through it for 15 minutes. Allow the precipitate to settle for 20 minutes, filter and wash with alcohol saturated with  $\text{H}_2\text{S}$ . Dry and ignite the precipitate, then dissolve the residue in 9 cc. of  $\text{HNO}_3$  (sp.gr. 1.42) by warming, add warm water to bring the volume to 50 cc., and electrolyze at 0.4 ampere and 2.5 volts, temperature 65° C., for 1 hour. Wash the electrode by replacing the beaker with another one containing distilled water without interrupting the current. Dry and weigh the previously tared anode. The weight of lead peroxide found  $\times 0.8661$  gives the percentage of soluble lead found.

**Nitric Acid.** No coloration should result when a water solution of picric acid is treated with a solution of diphenylamine in sulphuric acid.

### Ammonium Picrate

Ammonium picrate, also known in this country as "Explosive D," is of importance as a military explosive more on account of its insensitiveness to shock and friction, than because of its explosive strength, which is less than that of TNT. Its chief use is as a bursting charge in armor-piercing projectiles.

Military specifications require it to be prepared from picric acid of standard purity, to contain not less than 5.60% ammoniacal nitrogen, and not more than the following amounts of impurities:

Moisture .....	0.20%
Sulphuric acid (free and combined).....	0.10%
Nitrates .....	trace
Insoluble material .....	0.20%
Ash .....	0.20%
Nitrophenols ..	0.50%

**Moisture.** A sample of about 10 grams spread on a tared watch glass is dried at 95° C. to constant weight (about 2 hours).

**Sulphuric Acid.** About 5 grams is dissolved in 100 cc. of hot water, filtered, washed with 25 cc. hot water, the filtrate acidified with  $\text{HCl}$ , heated to boiling and treated with hot  $\text{BaCl}_2$  solution. Any precipitate is filtered on a weighed Gooch crucible, dried at 100° C., weighed and calculated as  $\text{H}_2\text{SO}_4$ .

**Nitrates.** A water solution of the sample tested with diphenylamine and  $\text{H}_2\text{SO}_4$  should give no blue coloration.

**Insoluble Material.** A 10-gram sample is boiled with 150 cc. of water for 10 minutes, filtered on a Gooch crucible, the residue washed with hot water, dried at 100° and weighed.

**Ash.** A sample of about 1 gram is saturated with melted paraffin and burned in a tared crucible, the residue ignited to burn off all carbon, and the ash weighed.

**Nitrophenols.** 10 grams of powdered sample is treated with 50 cc. of chloroform for 30 minutes with frequent stirring and filtered into a 100 cc. tared flask, the residue being washed with 25 cc. of chloroform. The filtrate is evaporated to dryness and any residue obtained weighed. This residue is treated with ammonium hydroxide, again evaporated to dryness and extracted the second time with 25 cc. of chloroform. The chloroform filtrate is evaporated to dryness and the residue weighed. The difference in weight between this residue and the first residue equals the nitrophenols, other chloroform-soluble having been eliminated by the ammonia treatment and second extraction.

### Tetryl

Tetryl is the commercial term applied to the explosive trinitrophenyl-methylnitramine, also improperly called tetranitromethylaniline. Its chief use is as a "booster" charge in high explosive shell, where it serves to transmit the detonating wave from the detonator or fuze to the less sensitive bursting charge. Being in immediate contact with the fuze it must be of a high degree of purity, and is required by Ordnance Department specifications to have a melting point of at least 128° C. and to contain not more than the following amounts of impurities:

Moisture.....	0.05%
Acidity (as H <sub>2</sub> SO <sub>4</sub> ).....	0.01%
Insoluble in acetone ..	0.30%
Ash.....	0.15%
Sodium salts ..	trace

**Melting Point.** The sample to be used for this test is dried overnight in a vacuum desiccator and pulverized to pass a 100-mesh screen. A capillary melting-point tube is filled to about  $\frac{1}{4}$  inch from the bottom and attached to the stem of a standard thermometer so that the sample is next to the center of the bulb. The bath is properly agitated and provision made for correcting for the emergent stem of the thermometer. The temperature of the bath is raised rapidly to 120° C., then at the rate of 1° in 3 minutes, the temperature at which the first meniscus appears across the capillary tube being noted as the melting point.

**Moisture.** A sample of about 10 grams is weighed in a wide shallow weighing bottle and dried over sulphuric acid in a desiccator for 24 hours, the sample being spread uniformly so that its depth is not over 0.5 cm. The loss of weight is regarded as moisture.

**Acidity.** A 10-gram sample, finely powdered, is shaken for 5 minutes with 50 cc. of boiled distilled water, filtered, washed with 50 cc. more water, and the filtrate and washings titrated with N/50 NaOH solution using phenolphthalein indicator.

**Insoluble in Acetone.** 10 grams of sample is dissolved in 75 cc. of acetone, filtered through a tared Gooch crucible, and the residue washed with 25 cc. of acetone, dried to constant weight at 100° C. and weighed.

**Ash.** The dried residue insoluble in acetone is ignited, cooled in a desiccator and weighed.

**Sodium Salts.** Any sodium present in tetryl is combined as sodium picrate, 10 grams of the tetryl are boiled in 50 cc. distilled water, cooled, filtered, the filtrate acidified with acetic acid and evaporated to 10 cc., cooled again and filtered. The filtrate is made alkaline with ammonia and treated with 5 cc. of 10% solution of ammoniacal copper sulphate. Any sodium picrate will be precipitated as crystals of cupro ammonium picrate on standing for a few minutes.

### Mercury Fulminate

In commercial blasting caps and electric detonators mercury fulminate is generally found intimately mixed with potassium chlorate. It is, however, used without admixture in certain types of detonators, in the fuzes of high explosive shell and for other military purposes. It is usually purchased under specifications which provide that it shall be at least 98% pure, shall be free from acid, and contain not more than 2% insoluble matter, 1% free mercury, and 0.05% chlorine in the form of chlorides.

**Preparation of Sample.** Mercury fulminate being packed and handled in a thoroughly wet condition until dried just before use, it is generally necessary to dry the sample before testing. This may be done by exposing in a low temperature oven at not more than 50° C. until practically dry, then in a desiccator (not a vacuum desiccator) over sulphuric acid or calcium chloride until its weight is constant.

**Mercury Fulminate Content.** Exactly 0.3 g. is weighed into a wide-mouthed Erlenmeyer flask containing 250 cc. distilled water, and 30 cc. of a 20% solution of purest sodium thiosulphate is added quickly and the mixture shaken for exactly 1 minute. At once titrate with N/10 hydrochloric acid using 3 drops of methyl orange indicator, the titration to be commenced 1 minute after adding the sodium thiosulphate, and to occupy not more than 1 minute additional time.

The percentage of mercury fulminate is calculated from the volume of standard acid required, after deducting the volume of acid required for a blank determination. Four molecules of HCl are equivalent to 1 mol. of mercury fulminate, or 1 cc. N/10 HCl equals 0.00711575 g. mercury fulminate. The reaction is assumed to be as follows:



**Acidity.** A 10-g. sample is extracted with 2 successive 25-cc. portions of boiled distilled water in a Gooch crucible, and 3 drops of methyl orange solution (1 g. per liter) added. No red tinge of color should be obtained.

**Insoluble Matter.** A 2-g. sample is dissolved in hot 20%  $\text{Na}_2\text{S}_2\text{O}_3$  solution, filtered through a tared Gooch crucible and any insoluble washed with water then with alcohol and finally with ether, dried at 60°–70° C. and weighed.

**Free Mercury.** The residue of insoluble matter obtained as described above is treated with a solution of 3 g. KI and 6 g.  $\text{Na}_2\text{S}_2\text{O}_3$  in 50 cc.  $\text{H}_2\text{O}$  by passing the solution through the Gooch crucible. Any organic mercury com-

pounds are thus converted into mercuric iodide, which is soluble in  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The metallic mercury remains behind on the filter, and is washed with  $\text{H}_2\text{O}$ , dried 1 hour at  $80^\circ\text{--}90^\circ\text{C}$ ., and weighed.

**Chlorides.** A 5-g. sample of fulminate is extracted in a Gooch crucible with 2 successive 25 cc. portions of distilled water at  $90^\circ\text{--}100^\circ\text{C}$ . Three drops of strong  $\text{HNO}_3$  and 10 drops of 10%  $\text{AgNO}_3$  solution are added to the filtrate. If a turbidity results, the  $\text{AgCl}$  should be determined gravimetrically or a fresh sample extracted and the filtrate titrated with a standard  $\text{AgNO}_3$  solution.

### Blasting Caps and Electric Detonators

**Preparation of Sample.** In the examination of blasting caps or detonators for either commercial or military use, the removal of the detonating composition from the copper or brass shell requires considerable precaution. Blasting caps are emptied by squeezing the cap gently in a pair of "gas forceps," the jaws of the forceps being passed through a small opening in a piece of heavy leather, rubber belting, or similar material, about 6" square, which serves as a shield to protect the hand in case of the possible explosion of the cap in squeezing. After each squeeze, the loosened portion of the charge is shaken out on a piece of glazed paper, the cap turned slightly in the forceps and again squeezed. The pressure on the cap should be just sufficient to slightly dent it, and in shaking out the charge, the cap should not be tapped on the table or other surface. With these precautions there is little danger of an explosion.

Electric detonators are opened by first cutting off the wires or "legs" close to the shell, then tearing off the upper portion of the shell by means of pointed side-cutting pliers, the cap being held firmly in the fingers and a thin strip of the copper shell being torn off spirally by nipping the top edge of the shell with the forceps. This must be done with great care, especially as the portion of the shell containing the fulminate charge is approached. When the greater portion of the plug which holds the wires in place has been exposed, the plug and wires are gently pulled out, care being taken to avoid force and possible friction, and any adhering particles of the charge brushed off onto glazed paper. The charge is then removed from the lower part of the shell just as in the case of blasting caps.

The charge is removed separately from several of the caps or detonators and each weighed in order to determine the average weight of charge as well as variation of same.

"Reinforced" caps, or those which contain a small perforated inner copper capsule pressed on top of the charge, must be opened in the manner described for electric detonators, in order to remove the inner capsule. Detonators of this type usually contain a main charge of some nitro compound superimposed by a layer of mercury fulminate, mixture of fulminate and chlorate, or lead azide. Although a clean mechanical separation of the two layers is usually not possible, portions can be taken from each and identified by qualitative tests before proceeding with a quantitative examination.

**Moisture.** The moisture content of the composition is determined by desiccating to constant weight over sulphuric acid or calcium chloride.

**Analysis of Composition Containing Mercury Fulminate and Potassium Chlorate.** About 2-3 grams of the well-mixed composition is weighed in a Gooch crucible provided with asbestos mat or disc of filter paper or silk, and first moistened with a few drops of alcohol, then extracted with 200-250 cc. of cold water in 15-20 cc. portions, using slight suction after each portion has remained in the crucible for a few minutes. The residue in the filter is dried to constant weight at 60°-70° C. (2-3 hours), and weighed.

The water extract contains the potassium chlorate and a portion of the mercury fulminate, which is slightly soluble in cold water. It is treated with 2 cc. of ammonium hydroxide and  $H_2S$  passed to completely precipitate the dissolved mercury fulminate as  $HgS$ . This black precipitate is filtered off, washed, dried and weighed. Its weight  $\times 1.22$  gives the amount of mercury fulminate dissolved by the water. This weight added to the weight of the dried residue insoluble in water gives the total weight of mercury fulminate in the sample. The  $KClO_3$  is found by subtracting the % of mercury fulminate + % moisture from 100%.

**Analysis of Compositions Containing Nitrocompounds.** Trinitrotoluene, tetryl or picric acid can be identified by melting point test, TNT. melting at about 79°-80° C., tetryl at about 128° C., and picric acid at about 120°-122° C. They may be extracted from the mixture by means of ethyl ether, in which mercury fulminate is only very slightly soluble, and the determination of  $KClO_3$  and mercury fulminate then made as described in the preceding paragraph.

If the main charge is an organic nitrate such as nitrated vegetable ivory, nitrostarch, etc., such material will be left with the mercury fulminate in the insoluble residue after extraction with water. The mercury fulminate is then extracted by means of a hot 20% solution of sodium thiosulphate, leaving the organic nitrate in the Gooch crucible. These materials in the detonating composition can be readily identified by microscopic examination.

In detonators where TNT. or tetryl compose the main portion of the charge, a small amount of lead azide, with or without mercury fulminate may be used as a priming charge for the purpose of initiating the detonation of the nitrocompound. It should be identified in the top portion of the charge, next to the reinforcing cap, and will in all probability be present if mercury fulminate is not found. It is practically insoluble in water and in ether, and will be left in the insoluble residue. If present, fulminate is destroyed by treating the residue, in a flask, with 25 cc. of KOH solution. This converts the lead azide to potassium azide,  $KN_3$ . A slight excess of  $H_2SO_4$  is added and the mixture distilled, the distillate, containing  $HN_3$ , being collected in water. Enough NaOH is added to the distillate to give an alkaline reaction with litmus, then a little  $Pb(NO_3)_2$ , when lead azide,  $PbN_6$  will be regenerated as a white precipitate, which may be filtered off, washed with water, then with alcohol, dried in the air, and tested by striking a small portion with a hammer.

## Primers

**Variations in Composition.** Many varieties of composition are used in primers for small arms ammunition, and for other military purposes. The composition must be ignited by the impact of the firing pin, and must give a flame of sufficient intensity and duration to ensure proper ignition of the propellant or of the detonator, depending on the purpose for which the primer is employed. As primers are used with various kinds and granulation of explosives, a priming composition suitable for one purpose is unsuited for another; hence there are many types of priming compositions, a few of which are indicated in the following table:

**TYPES OF PRIMER COMPOSITIONS**  
**APPROXIMATE COMPOSITION (PER CENT)**

Ingredients	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10
Mercury fulminate...	31	25	11							28
Potassium chlorate.....	38	38	53	60	50	51	53	■	47	14
Sulphur.....				7	3	9			22	
Powdered glass.....						12				35
Lead sulphocyanate.....							25	25		
Copper sulphocyanate.....				3						
Barium nitrate.....		6								
TNT.....							5			
Tetryl.....								3		
Antimony sulphide.....	31	31	36	30	44	26	17	17	31	21
Lead oxide (PbO).....								2		
Shellac.....						■				2
Black powder (meal).....					3					

In addition to these ingredients most priming compositions are mixed with small amounts of some binding material dissolved in water or alcohol, such as gum arabic, gum tragacanth, glue, shellac, etc. These traces of binding materials are usually disregarded in the analysis of the compositions.

**Preparation of Sample.** If the caps contain anvils, these must first be carefully removed, as well as any covering of tin foil or paper. The primer composition is then carefully removed from a number of primers and weighed to determine the average charge. It is then carefully crushed, a little at a time, and the sample well mixed. If necessary, it may be removed from the caps by the aid of water or alcohol and the latter removed by evaporation before weighing.

**Qualitative Examination.** The following special tests may be made use of in connection with a qualitative analysis of the mixture:

A small amount is burned between two watch glasses, the formation of a mirror indicating mercury, antimony, copper or lead. The mercury mirror is readily volatile on gentle ignition.

Extract a portion of the mixture with ether, then with water, then with  $\text{Na}_2\text{S}_2\text{O}_3$  solution, then with aqua regia, retaining each of these solutions.

TNT. or tetryl may be present in the ether solution and are identified by m.p. or color test, TNT. giving a deep red color with acetone and KOH. Sulphur is detected by burning a portion of the ether-soluble material and noting odor of  $\text{SO}_2$ .

The water extract is tested for  $\text{KClO}_3$  by adding  $\text{H}_2\text{SO}_4$ , boiling, and noting odor of chlorine. A portion is treated with  $\text{HCl}$  and  $\text{FeCl}_3$ , a red color indicating thiocyanate. The usual  $\text{FeSO}_4$  ring test is made for nitrates. A white precipitate with  $\text{H}_2\text{SO}_4$  indicates Ba or Pb.

The aqua regia solution is diluted and tested with  $\text{H}_2\text{S}$  for antimony, lead, and copper. If the precipitate is not orange-red, lead or copper are indicated. Dissolve in  $\text{HNO}_3$ , neutralize with  $\text{NH}_4\text{OH}$ ; a blue solution indicates copper, while lead is detected by the formation of a white precipitate with  $\text{H}_2\text{SO}_4$ .

Any material insoluble in aqua regia may be powdered glass or other abrasive material.

**Quantitative Analysis.** The method of analysis will depend entirely upon the ingredients indicated by qualitative tests. In general, a separation is best effected by successive extractions with ether, water,  $\text{Na}_2\text{S}_2\text{O}_3$  solution (to remove fulminate), dilute or concentrated  $\text{HCl}$ , and aqua regia. The small amount of mercury fulminate present in the water extract may be determined by precipitation with  $\text{H}_2\text{S}$  or by adding 10–15 cc. of thiosulphate solution and a few drops of methyl orange and titrating with  $\text{N}/10$   $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  (see page 513 of Vol. I). Other materials in the water and acid solutions are determined by the usual analytical methods.

### Nitrocellulose

**General.** The term nitrocellulose, or more correctly cellulose nitrate, applies to any nitration product of cellulose, ranging from products containing in the neighborhood of 10–11% N, which are used in the preparation of lacquers and other commercial products, to military guncotton with over 13% N. All of these products are undoubtedly mixtures of the various nitrates of cellulose, as indicated by the fact that there is always some material with low nitrogen content, soluble in ether-alcohol, in high nitrogen guncotton, and some insoluble material in the lower nitrated commercial products. It can usually be shown without great difficulty that any nitrated cotton is a mixture of various nitrates of cellulose.

The products of military importance are the insoluble guncotton of high N-content, and the so-called "pyro" or pyrocellulose, soluble in ether-alcohol and of about 12.60% N-content. In testing these products, the characteristics of most importance are content of nitrogen, solubility in ether-alcohol, and stability. Other determinations generally made are solubility in acetone and ash.

**Preparation of Sample.** If the sample contains a large excess of water, it is enclosed in a clean cloth and the excess water removed by means of a press or wringer. The pressed sample is then rubbed up in the cloth (not with the bare hand) until lumps are removed, then spread on clean paper trays in an air bath at about 35°–40° C. until "air-dry."

Samples for stability tests and nitrogen determination are treated as noted below, the air-dry sample being suitable for determining solubility and ash.



**Nitrogen.** About 1 to 1.05 g. of the air-dry sample is roughly weighed in a tared weighing bottle, dried at 95°–100° C. for 1½ hours, cooled in a desiccator and accurately weighed. It is then transferred to the generating bulb of a nitrometer (Du Pont modification; see p. 354) using a total of 20 cc. of 95–96% c.p.  $H_2SO_4$ . The sample must be dissolved in the acid either in the weighing bottle or in the cup of the generator, before it is drawn into the generating bulb, and both the weighing bottle and the cup of the generator must be thoroughly washed out with the 20 cc. of  $H_2SO_4$ , so that none of the sample is lost. The determination in the nitrometer is completed in the usual manner (p. 354), the result being expressed as % N in the dried sample of nitrocellulose.

**Solubility in Ether-Alcohol.** (a) *Guncotton*: The amount of ether-alcohol soluble material in guncotton being usually not more than 10–12%, the determination may be made by evaporating a clear solution. Two grams of air-dry sample is placed in a clean dry cork-stoppered 250 cc. cylinder, 67 cc. of 95% ethyl alcohol added to thoroughly wet the guncotton, then 133 cc. of ethyl ether (U.S.P. grade, 96%), added and the mixture well shaken. If the mixture of 2 parts ether and 1 part alcohol be added at once to the sample, a gummy mass may result which dissolves with great difficulty, especially if the solubility is unusually high.

The cylinder is now allowed to stand at a constant temperature of usually 20° C. (15.5° C. is sometimes specified). The solubility of nitrocellulose increases as the temperature is decreased, hence a constant temperature of digestion is important. During the digestion, which requires at least 1 hour, the cylinder must be thoroughly shaken at 5-minute intervals. The cylinder is now allowed to stand for at least 4 hours, until the insoluble portion of the sample has completely settled and the supernatant liquid is perfectly clear.

50 cc. of the clear solution is now drawn off with a pipette, care being taken not to disturb the settled pulp, and evaporated in a weighed evaporating dish on a steam bath, avoiding loss from violent boiling of the ether. When 25–30% of the solution has been evaporated, 10 cc. of distilled water is added slowly and the evaporation continued to dryness. The effect of the water is to leave the residue in a white, brittle or powdery condition, rather than a tough film which would lose its solvent with difficulty.

The dish is finally placed in an oven at 95–100° C. for ½ hour, cooled in a desiccator, and weighed. The weight of the residue, corrected for the residue in the 50 cc. of ether-alcohol and 10 cc.  $H_2O$  used, represents the soluble nitrocellulose in 0.5 g. of the guncotton.

(b) *Pyrocellulose*: The solubility of pyrocellulose may be determined in the manner described for guncotton, but owing to the much larger amount of soluble material present, the evaporation of the residue to constant weight without decomposition involves considerable difficulty. Sufficient water must be added to precipitate the soluble nitrocellulose from solution in a stringy or fibrous condition.

The determination is usually conducted by either the volumetric method or the filtration method.

In the volumetric method, one gram of the air-dry sample is covered with 100 cc. of 95% ethyl alcohol and allowed to stand at least 15 minutes with frequent stirring, 200 cc. of ethyl ether is then added with stirring and the agitation continued until solution is complete. The solution is now allowed to stand at least 4 hours with frequent stirring, during at least 1 hour of which

time it is to be kept at a temperature of 15.5° C. It is then transferred to a "solubility tube" and allowed to stand for at least 16 hours, in order that the insoluble material may settle completely. The solubility tubes are glass tubes about 30.6 inches long  $\times$  1.3 inches inside diameter, tapering at a point 8 inches from the bottom to a constricted portion about 3 inches long and about .375 inch inside diameter. This narrow bottom portion is graduated to read directly the percentage of insoluble material, the value of the graduations having been first ascertained by comparison with results obtained by the filtration method described below. The tubes are made of heavy glass and provided with vented ground glass stoppers. They hold 300 cc. when filled to about 8 inches below the top.

In the filtration method, the solution is prepared and settled in a solubility tube as described above, and the clear liquid removed as completely as possible by means of a narrow siphon tube of glass. Fresh alcohol and ether are then added as before, the tube shaken and allowed to stand again for 16 hours, when the process may be repeated several times, depending on the amount of insoluble material present. After the last decantation, the residue is washed from the tube to a beaker, using as small a quantity of ether-alcohol as possible, and the mixture filtered through a filtering tube consisting of a 1"  $\times$  6" test tube with its lower end drawn out to a taper terminating in a hole about  $\frac{1}{8}$ " diameter. In the lower end of this tube is a small plug of previously ignited asbestos. The filtration is facilitated if the greater part of the asbestos is mixed with the insoluble matter and solvent in the beaker, the mixture well stirred and quickly poured into the filtering tube on top of a small plug of asbestos. In this manner, the insoluble matter becomes mixed with the asbestos and the formation of a gelatinous, impenetrable mat in the tube is avoided. After filtering, the tube is washed with fresh ether-alcohol, dried at 40°–45° C. and finally for 1 hour at 100° C., then cooled in a desiccator and weighed. All combustible matter is then removed by careful ignition, and the tube again weighed, the loss of weight being the total insoluble material in the 1-gram sample.

**Solubility in Acetone.** A 1-gram sample of air-dry pyrocellulose is treated with about 200 cc. of acetone with frequent stirring until all gelatinous matter has dissolved. The solution is transferred to a solubility tube (described above), the volume made up to about 300 cc. with fresh acetone, well shaken, and allowed to settle for at least 16 hours. The graduations on the tube having been checked by gravimetric determinations, the percentage of residue insoluble in acetone may be read direct, or the filtration method described above may be applied.

**Ash.** One gram of air-dry sample is weighed in a tared crucible, moistened with 10–15 drops of concentrated nitric acid, and digested for 2–3 hours on a steam bath until converted to a gummy mass. The crucible is then heated carefully over a Bunsen burner until the mass is completely charred, then at a red heat until its weight is constant. The residue is the ash of the sample.

**Stability Test: Heat test with Potassium Iodide Starch Paper.** The "heat test" or KI test, as it is commonly designated, is the test most commonly employed for determining the stability or degree of purification of nitrocellulose, whether guncotton or pyrocellulose. This test, also referred to as the Abel test, depends on the action of oxides of nitrogen liberated by the nitrocellulose under the influence of heat, the gases in contact with the KI-starch paper liberating iodine which colors the starch.

The sample is dried with great care to avoid contamination, in a clean paper tray, at 35° to 43° C., until its moisture is reduced to the amount which will give the minimum heat test, usually 1.5 to 2%. The proper amount of moisture is determined as follows: During the progress of the drying, the sample on the tray is "rubbed up" from time to time, using a piece of clean tissue paper spread over the back of the hand. When the sample begins to adhere to the paper, due to static electricity, a sample of 1.3 g. is weighed into a standard test tube. These tubes are 5½ inches long, not less than ½ inch inside diameter and not more than ¾" outside diameter, made of glass about 3/64 inch (1.2 mm.) thick. As soon as the first sample is weighed, the tray is replaced in the drying oven for 2-5 minutes, a second sample weighed, and this process repeated until a series of 5 samples have been taken, the last sample being completely dry. This series of samples, if properly taken, will cover the range of moisture content giving the minimum heat test. If the sample in the tray appears to have become too dry during the time the weighings are being made, it may be placed in a moist atmosphere for not more than 2 hours; the entire time of drying and making the test must not exceed 8 hours.

The tubes containing the samples are fitted with clean, fresh cork stoppers through which pass a piece of glass rod into the end of which is fused a small piece of platinum wire bent into a hook. The wire is heated in a flame to clean it, a piece of the standard KI starch test paper, 1" × ¾", attached, taking care that neither wire nor paper are touched with the fingers, and the paper moistened on its upper portion by touching it with a glass rod dipped in a solution of equal volumes of pure glycerin and water. The stoppers are then inserted in the tubes and the tubes placed in a constant temperature water bath, so that they are immersed to a depth of 2.25 inches. The time of placing in the bath and the time of the appearance of the first faint yellowish discoloration of the test paper are noted. The minimum test given by the 5 samples is taken as the result of the test. The discoloration appears at the lower edge of the moist portion of the paper. The temperature of the heat test bath is 65.5° C. (150° F.) for pyrocellulose, and usually 76.5° C. (170° F.) for guncotton. Pyro is usually required to stand a test of 35 minutes, and guncotton 10 minutes.

A standard test paper is absolutely essential, and is prepared as follows:<sup>1</sup>

The paper used in preparing the test paper is Schleicher and Schüll's filter paper 597. This is cut in strips about 6 by 24 inches, and after being washed by immersing each strip in distilled water for a short time is hung up to dry overnight. The cords on which the paper is hung are clean and the room is free from fumes. The washed and dried paper is dipped in a solution prepared as follows:

The best quality of potassium iodide obtainable is recrystallized three times from hot absolute alcohol, dried, and 1 gram dissolved in 8 ounces of distilled water. Cornstarch is well washed by decantation with distilled water, dried at a low temperature, 3 grams rubbed into a paste with a little cold water, and poured into 8 ounces of boiling water in a flask. After being boiled gently for 10 minutes, the starch solution is cooled and mixed with the potassium iodide solution in a glass trough.

<sup>1</sup> Storm, C. G., Proc. 7th Inter. Congress Appl. Chem., 1909; J. Ind. & Eng. Chem., vol. 1, 1909, page 802.

Each strip of filter paper is immersed in the above-mentioned mixture for about 10 seconds and is then hung over a clean cord to dry. The dipping is done in a dim light and the paper left overnight to dry in a perfectly dark room. Every precaution is taken to insure freedom from contamination in preparing the materials and from laboratory fumes that might cause decomposition. When dry the paper is cut into pieces about  $\frac{3}{8}$  by 1 inch and is preserved in the dark in tight glass-stoppered bottles, the edges of the large strips being first trimmed off about one fourth inch to remove portions that are sometimes slightly discolored. When properly prepared the finished paper is perfectly white, any discoloration indicating decomposition due to contamination.

**Stability Test at 135° C.** In addition to the KI starch test, pyrocellulose is usually required to stand a test at 135° C., made as follows:

The sample is completely dried at 42° C., and 2.5 grams placed in each of 2 heavy glass tubes, 290 mm. long, 18 mm. outside diameter and 15 mm. inside diameter, closed with a cork stopper through which passes a hole 4 mm. in diameter. A strip of litmus paper or standard normal methyl violet paper, 70 mm. long and 20 mm. wide is placed in each tube, its lower edge 25 mm. above the sample, which is pressed down to occupy a depth of 2 inches, the walls of the tube being wiped clean with a roll of paper. The tubes are then heated in a constant temperature bath at 134° to 135° C., all but about 6-7 mm. of the tube being immersed in the bath. They are partially withdrawn for examination of the test papers every 5 minutes after the first 20 minutes of heating, and replaced at once. The time required for reddening of the litmus paper or for turning the methyl violet paper to a salmon pink color is noted as the time of the test. A minimum test of 30 minutes is required with the methyl violet paper, and heating is then continued for a total of 5 hours, during which time there should be no explosion.

The standard normal methyl violet paper is prepared as follows:

**Preparation of Methyl Violet Test Paper.** A solution is prepared containing the following ingredients: pure rosaniline acetate prepared from 0.2500 g. basic rosaniline, .1680 g. methyl violet (crystal violet), 4 cc. c.p. glycerin, 30 cc. water, and sufficient pure 95% ethyl alcohol to make up to 100 cc. This solution is placed in the angle of an inclined deep rectangular glass tray, and large sheets of Schleicher & Schüll filter paper (No. 597) cut in four strips are dipped in it. In dipping, the strip is held by one end and dipped to within  $\frac{1}{4}$ " of this end, withdrawing it slowly up the side of the tray so as to remove surplus solution. The strip is then held horizontally and waved to and fro so as to prevent the solution from running and collecting in spots. As soon as the alcohol has evaporated the strip is suspended vertically to dry, and when dry is cut in strips 20×70 mm. These strips are bottled and kept for use in the 135° test.

## SMOKELESS POWDER

### Nitrocellulose Powders

At the present time the smokeless powder used by all nations is composed of either colloided nitrocellulose alone or a mixture of colloided nitrocellulose and nitroglycerin. All cannon powder used in this country is of the nitrocellulose type, small-arms powders being of both types. The form and size of the grains are of great variety, depending on the arm in which the propellant is to be employed.

Physical tests made in connection with the examination of smokeless powder include the compression test, determinations of average measurements of the grains, specific gravity, gravimetric density, number of grains per pound, and calculation of burning surface per pound.

Chemical tests include determinations of moisture and volatile solvent, diphenylamine used as stabilizer, ash, material insoluble in ether-alcohol and in acetone, and sometimes nitrogen content.

Stability tests include the 135° C. test, the 115° C. test, and the "Surveillance test."

**Moisture and Volatiles.** A sample of the powder weighing approximately 1 gram, in the form of thin shavings cut from at least 10 grains, or of whole grains if the powder is too small to cut conveniently, is placed in a clean, dried and weighed 250 cc. beaker, 50 cc. of redistilled 95% (by volume) alcohol, and 100 cc. redistilled ethyl ether added and the beaker allowed to stand under a cover-jar with occasional stirring, until the powder is completely dissolved. This usually requires from 1 to 2 days. When all gelatinous particles of the powder have dissolved, the beaker is heated on the steam bath to evaporate a part of the ether, before precipitation of the nitrocellulose with water. The amount of ether to be evaporated is important, since it largely determines the character of the nitrocellulose precipitate. The presence of too much ether causes a fine sandy precipitate; too little causes a gummy, gelatinous precipitate. A fine, flaky, or fibrous precipitate is desirable. The proper amount of evaporation can be best determined by practice; usually the solution may be evaporated to about  $\frac{2}{3}$  its original volume before precipitating. When the proper volume is obtained, 50 cc. of water is added from a graduate, with continual stirring, in 5 cc. portions. If a thick gummy precipitate forms, add a little ether until it becomes flaky; then add the remainder of the 50 cc. of water. The heating is continued with stirring, until most of the ether has evaporated, and the beaker is then left on the bath until the precipitate is just dry. It is then placed in the 100° C. oven for 1 hour, cooled in a desiccator, and weighed as rapidly as possible. To facilitate weighing the weights should be placed on the balance pan before the beaker is removed from the desiccator, so that the exact weight can be adjusted quickly. If more than 10 seconds are consumed in this weighing, the error caused by absorption of moisture from the air is an appreciable one. In any event a check weighing should be made after an additional 30 minutes drying at 100° C.

The final weight of nitrocellulose precipitate subtracted from the weight of the original sample represents the weight of moisture and volatile solvent, and is calculated as per cent of the original sample. If the powder contains diphenylamine, this result is corrected by subtracting from it one fourth of the total diphenylamine content, it having been ascertained by actual trial that

approximately this proportion of the diphenylamine is volatilized during the evaporation.

**Moisture.** An approximation to the actual moisture content of the powder can be obtained by drying a sample of not less than 5 whole grains and not less than 20 grams for 6 hours at  $100^{\circ}\text{C}$ ., cooling in a desiccator and weighing, the loss of weight being regarded as equal to the hygroscopic moisture in the powder.

**Diphenylamine.** The content of diphenylamine used as a stabilizer in smokeless powder is most conveniently and rapidly determined by the "nitration method" as follows:

5 grams of the powder in small grains or slices is treated with 30 cc. of concentrated  $\text{HNO}_3$  in a 250 cc. beaker, covered with a watch glass and heated on the steam bath until the powder has been completely decomposed. The solution is then cooled and added to 100 cc. of cold distilled  $\text{H}_2\text{O}$  in a second beaker, stirring vigorously, the first beaker being washed out completely into the second, using additional water. This mixture is now heated on the steam bath until the flocculent precipitate has settled and the liquid has a clear yellow color. It is then cooled, filtered through a weighed Gooch crucible, the precipitate dried at  $100^{\circ}\text{C}$ . and weighed. The weighed precipitate is now dissolved by extracting with acetone, the crucible dried and weighed again, the loss of weight being the nitrodiphenylamine produced by action of the  $\text{HNO}_3$  on the diphenylamine. This nitrodiphenylamine is a mixture of nitroproducts, and the empirical factor 0.40576 has been determined for converting it to its equivalent in diphenylamine.

**Ash.** The ash is determined in the manner described for nitrocellulose (p. 1401), the sample being in the form of slices or small grains, and the digestion with  $\text{HNO}_3$  continued until decomposition is practically complete, before heating over a flame.

**Solubility in Ether-alcohol.** One gram of the sample in slices or small grains is dissolved in 150 cc. of ether-alcohol (2 : 1) in the same manner as for the determination of moisture and volatiles, and transferred to a standard solubility tube (p. 1401), washing it in completely with fresh ether-alcohol so as to bring the total volume to 300 cc. The insoluble material is determined as in pyrocellulose (p. 1401).

**Solubility in Acetone.** This determination is made in the same manner as the solubility in ether-alcohol, described above.

**Stability Test at  $135^{\circ}\text{C}$ .** This test is made on duplicate samples in the same manner as described for pyrocellulose (p. 1403). The samples weigh 2.5 grams and are in as nearly whole grains as is consistent with this weight of sample, large grains being turned down on a lathe to fit the standard tubes. The samples are required to stand heating at  $134^{\circ}$ – $135^{\circ}\text{C}$ . for 5 hours without explosion and must not turn the normal methyl violet paper to salmon pink color in less than one hour.

**Stability Test at  $115^{\circ}\text{C}$ .** This test is also known as the Ordnance Department  $115^{\circ}$  test, or the Sy test. Five samples each consisting of not more than 10 grams and not less than 2 whole grains of the powder are weighed on watch glasses and heated at a temperature of  $115^{\circ} \pm 0.5^{\circ}\text{C}$ . for 8 hours daily for 6 days, the oven being brought each day to the proper temperature before the samples are inserted, the samples being allowed to stand at room conditions overnight. At the end of the sixth day's heating, the samples are cooled in a

desiccator and weighed. The total loss of weight is regarded as an index of the stability, and must not exceed a specified limit for each particular size of grain.

**"Surveillance Test"** at  $65.5^{\circ}\text{C}$ . Three samples of approximately 45 grams of powder in whole grains, or, in the case of very large grains, 5 whole grains, are placed in 8-ounce wide-mouth glass stoppered bottles, the stoppers having been previously ground so as to fit tightly. These bottles are then heated in a constant temperature magazine at  $65.5^{\circ} \pm 2^{\circ}\text{C}$ . They are observed several times daily and the time noted when visible fumes of oxides of nitrogen appear in any bottle. The number of days which powder is required to stand this test depends on the web thickness of the grain, and varies from 70 to 140 days. The test is therefore not a laboratory test, but one which more nearly approaches service conditions. It is of great value as an indication of the possible "stability life" of the powder in service.

**Nitrogen.** The determination of nitrogen in smokeless powder is not usually necessary, in as much as the powder is usually made from nitrocellulose of known nitrogen content, but when desired the determination is made as follows:

An average sample of about 5 grams of the powder in slices or small grains is dissolved in acetone (100 cc. to each 1 g. of sample). When the sample is dissolved, the solution is added drop by drop, preferably from a burette, to 200 cc. of hot water in a beaker, the beaker being immersed in boiling water so as to maintain its contents at about  $90^{\circ}\text{C}$ . During this addition the hot water is continually stirred with a glass rod, so that the precipitated nitrocellulose forms stringy masses which wrap about the rod. Small accumulations of the precipitate are transferred frequently from the rod to another beaker of hot water to prevent the formation of a colloided mass. When 2 g. or more of the precipitate has been collected and the acetone has been volatilized by the hot water, it is removed from the beaker and dried at  $35^{\circ}\text{--}40^{\circ}\text{C}$ . About 1 g. of this dry precipitate is placed in a tared weighing bottle, dried 1 hour at  $100^{\circ}\text{C}$ ., weighed, and transferred to the cup of the nitrometer with sulphuric acid. Part of the acid should be added to the precipitate in the weighing bottle before transferring to the nitrometer in order to avoid loss of the dry precipitate in handling. The determination of N is then completed as in the case of nitrocellulose (page 1400). If the powder contains diphenylamine, a correction is necessary for the amount of diphenylamine retained by the precipitated nitrocellulose. This has been found to be an added correction of 0.15% N in the case of powders containing the usual amount of 0.4% diphenylamine. This correction compensates for the nitrogen which becomes combined with the diphenylamine, converting it to nitrodiphenylamines.

Instead of correcting for the effect of the diphenylamine, the latter may be removed from the precipitated nitrocellulose, after air-drying and before final drying at  $100^{\circ}\text{C}$ ., by extraction with pure anhydrous ether. Results are quite accurate if the determination is conducted with proper precaution.



### Nitroglycerin Smokeless Powders

Powders of this type are composed mainly of nitrocellulose and nitroglycerin and may contain other organic or inorganic substances, such as vaseline, nitro-substitution compounds, substituted ureas or other flame-reducing or surface-hardening agents, diphenylamine, metallic nitrates, carbonates, etc. The nitrocellulose may be either high-nitration guncotton insoluble in ether-alcohol, as in British cordite, or a low-nitration product soluble in nitroglycerin, as in ballistite, or may be a mixture of the two varieties.

The method of analysis usually employed consists of (1) an extraction of the nitroglycerin, nitrosubstitution compounds, vaseline, and other ether-soluble materials by means of anhydrous ether; (2) an extraction of the water-soluble materials; (3) determination of soluble and insoluble nitrocelluloses by separation with ether-alcohol (2 : 1).

The extraction with ether is usually made in a Soxhlet apparatus, using about 20 grams of the powder in slices or small grains, in a paper extraction thimble. About 4 hours is usually required for complete extraction. The ether extract is evaporated to dryness in a tared glass dish under a bell-jar evaporator (page 1376), and the ether-soluble residue weighed. To determine whether it contains other substances than nitroglycerin, it may be poured in small portions at a time into about 20 cc. of strong nitric acid (40° Be) heated on a steam bath. The oxidizing action of the nitric acid destroys the nitroglycerin, and the mixture is then poured into 50–100 cc. of water. Any vaseline or similar substances separate, together with any nitrosubstitution compounds in their original condition or more completely nitrated, diphenylamine in the form of a nitroderivative, etc.

These materials may be separated with more or less completeness by fractional crystallization from ether or other solvent. The exact method to be followed depends on the nature of the materials present.

The residue insoluble in ether is dried and weighed, and then transferred to an Erlenmeyer flask and digested in warm water until any water-soluble materials present have been dissolved. The mixture is filtered, the residue washed with hot water, dried and weighed. The filtrate containing the water-soluble ingredients is examined by the usual analytical methods for inorganic ingredients.

The nitrocellulose insoluble in water is tested for nitrogen content, solubility in ether-alcohol and solubility in acetone, by the methods already described.



## TYPICAL COMPOSITIONS OF COMMONLY USED EXPLOSIVES

*Black Blasting Powder*

Sodium nitrate.....	73
Charcoal.....	16
Sulphur.....	11 (Bu. of Mines, Bull. No. 80, p. 19.)

*Black Military Powder*

Potassium nitrate.....	75
Charcoal.....	15
Sulphur.....	10

*Typical Dynamite formulas—40% grades (Bu. Mines, Bull. No. 80, p. 21).*

	Nitro- glycerin	Nitro- Substi- tution Com.	Ammo- nium Nitrate	Sodium Nitrate	Nitro- cellu- lose	Wood Pulp	Cal- cium Car- bonate
40% straight Nitroglycerin Dynamite	40	.....	.....	44	.....	15	1
"40%-strength" Ammonia Dynamite	23	.....	20	42	.....	14	1
"40%-strength" Gelatin Dynamite.	33	.....	.....	52	1	14	1
"40%-strength" Low-freezing Dyna- mite.....	30	III	.....	44	.....	15	1
"40%-strength" Low-freezing Ammonia Dynamite.....	17	4	20	44	.....	13	1

*Granulated Nitroglycerin Powder ("Judson Powder",*

Nitroglycerin.....	5	10
Combustible material†.....	35	26
Sodium nitrate.....	60	64

## COAL MINING POWDERS. (PERMISSIBLE TYPE)

	I	II	III	IV	V	VI
Nitroglycerin.....	25	15	10	.....	.....	10
TNT.....	.....	5	.....	5	.....	.....
Ammonium nitrate.....	.....	.....	79	90	94	70
Sodium nitrate.....	34	44	.....	.....	.....	9
Sodium chloride.....	.....	.....	.....	.....	.....	10
Wood pulp.....	15	12	10	.....	.....	.....
Flour.....	25	17	.....	5	.....	.....
Aluminum powder.....	.....	.....	.....	.....	1	.....
Charcoal.....	.....	.....	.....	.....	3	.....
Calcium carbonate.....	1	1	.....	.....	.....	1
Zinc oxide.....	.....	.....	1	.....	.....	.....
Magnesium sulphate, cryst.	.....	15	.....	.....	.....	.....

\* Sometimes contains also flour, cornmeal, sulphur, etc.

† Composed of sulphur, coal, and rosin.

# WATER ANALYSIS

D. K. FRENCH<sup>1</sup>

Probably at no other time has the importance of a water supply, either for domestic or industrial purposes, been so great, as in these early years of the twentieth century. The increasing realization of the effect of contaminating materials, both organic and inorganic, on a municipal or private drinking supply—and history's record of the devastating nature of epidemics due to water-borne disease organisms, have led to the careful investigation of water for its sanitary value and the development of materials and equipment to fight and eliminate such contamination, and have increased many hundreds of per cent the factor of safety to the public health. In like manner, and even to a greater extent, has the value of water for industrial uses been a matter for careful consideration. It is hard for the public to realize the immense quantities of water used for industrial purposes, not only for the development of steam and electric power, but also for purposes of manufacture.

From the standpoint of power development we are familiar with the heat losses and the increased operating expenses due to scale formation in the steam or locomotive boiler, and also to the continued rapid decrease in valuation of boiler property, or of power plant property, due to corrosion or rusting. Another element of trouble which is noticed not so much in stationary boiler practice as in locomotive boiler practice, is the element of foaming and priming of a water, which results in much more rapidly putting the steam raiser out of active service than either of the other types of trouble.

From the standpoint of plant deterioration due to rusting and corrosion one has only to look to the great mass of works on the corrosion of iron and steel which are largely results of the growing need for some information as to the cause and possible prevention of this particular phase of trouble.

In the world of industry the action of a hard water upon soap consumption has been known for centuries, and for a considerable period of time the value of a water was determined largely by the amount of soap that it would consume and render insoluble. This same hardness has a noticeable effect in the textile industry, in bleaching and dyeing, in the canning industry, especially when the water supply contains such substances in large quantities. In the photographic industry the presence of chlorides in water and certain alkalies is a source of considerable trouble, and in every case, before any intelligent effort can be made to overcome these troubles, a complete analysis of the water is necessary.

It shall be our purpose in the methods which follow to give, where it is possible, first a system of analysis whereby a complete analysis can be made, and to follow this up with optional methods which, individually, are equally as good as those occurring in the system of analysis, and in some cases more satisfactory where the laboratory has the required equipment, adding any special methods which may be found available.

<sup>1</sup> Director of Laboratory, Dearborn Chemical Co.

## SANITARY ANALYSIS

A sanitary analysis consists in the physical examination covering turbidity, color, odor and occasionally taste, the chemical analysis for total residue, loss on ignition and fixed solids, noting, where possible, the odor during ignition and also noting the appearance as regards color of the residue both before and after ignition, the determination of free and albuminoid ammonia, nitrogen as nitrite and nitrate, chlorine as chloride and oxygen consumed. Organic nitrogen is frequently determined upon polluted waters.

In sanitary analysis the principal determinations relate to the various forms and compounds in which nitrogen appears.

**Organic Nitrogen.** The initial form can be determined as such, or as is usually the case in all but highly polluted supplies, as albuminoid ammonia which gives a very close approximate. By decomposition the organic matter first gives nitrogen as free ammonia, then, by oxidation, nitrogen as nitrites, and finally the more stable form of nitrogen as nitrates is reached. Conversely the reactions are frequently reversed through the influence of bacteria and microscopic organisms.

**Chlorine** is determined and by its excess over the normal chlorine of a general district may indicate previous sewage contamination.

**Oxygen Consumed**, or "oxygen required," means the amount which carbonaceous organic compounds present consume in the presence of potassium permanganate and acid. From these figures additional evidence is obtained as to the sanitary character of a water, though many phases of interference can occur.

## PHYSICAL TESTS

For the physical examination, standards for turbidity and color have been adopted.

**Turbidity.** Turbidity standards are based on parts per million of silica ( $\text{SiO}_2$ ) suspended in water, and the adopted standard is that of the United States Geological Survey (A. P. H. A., p. 4). A water with a turbidity of 100 is one which has 100 p.p.m. of silica ( $\text{SiO}_2$ ) in such a state of fineness that a bright platinum wire 1 mm. in diameter can just be seen when center of said wire is 100 mm. below the surface of the water and the observer is 1.2 meters above the wire. The observation must be in open air, not in sunlight, and in the middle of the day. Standards are prepared with precipitated fuller's earth (to pass 200-mesh sieve). One gram to one liter of distilled water makes a stock solution with 1000 turbidity. Standards for comparison are obtained by dilution.

The Illinois Water Supply Association outlines another method (Proc. - I. W. S. A., 1914, pp. 49-51), whereby a suspension is prepared by shaking silica ( $\text{SiO}_2$ ) or fuller's earth (ground to pass a 200-mesh sieve), settling for ten hours, and determining by evaporating and weighing the amount of silica ( $\text{SiO}_2$ ) in a given portion. Standards are then prepared by dilution.

**Color.** All suspended matter should be removed by filtration. The standard designated as color 500 is obtained as follows:

1.246 grams potassium platonic chloride ( $\text{PtCl}_2\text{2KCl}$ )<sup>1</sup> containing 0.5 gram of platinum and 1 gram crystallized cobalt chloride ( $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ ) containing 0.25 gram cobalt (Co), are dissolved in water with 100 cc. hydrochloric acid and made to one liter with distilled water. This solution is diluted with distilled water for comparative purposes, but a water with a color greater than 70 should be diluted prior to comparison. The standards for observation should be in 100-cc. Nessler tubes with the mark 20–25 cm. above the bottom and should be viewed vertically downwards to a white reflective surface.

Standard glass disks are used by the United States Geological Survey <sup>2</sup> in place of the above standard.

**Odor.** Observations should be made both on cold and hot samples. Note should be made immediately on opening containers as some odors are very transient and rapidly disappear.

**Cold.** Shake sample violently in collecting bottle, same to be about half full. Remove glass stopper and smell at neck of bottle.

**Hot.** Use either open beaker, 400 cc., containing 150 cc. sample well covered and heated nearly to boiling, or sealed glass stoppered bottle or saponification flask, heating fifteen minutes just under boiling. Allow to cool slightly, remove stopper, shake and smell. Designate odor as aromatic, grassy, earthy, musty, fishy, putrid, disagreeable, peaty, sweetish, etc. The following table expressing intensity of odor is copied from the American Public Health Association Standard Methods, 1913, p. 12:

Numerical Value.	Term.	Approximate Definition.
0	None.	No odor perceptible.
1	Very Faint.	An odor that would not be detected ordinarily by the average consumer, but that could be detected in the laboratory by an experienced observer.
2	Faint.	An odor that the consumer might detect if his attention were called to it, but that would not attract attention otherwise.
3	Distinct.	An odor that would be detected readily and that might cause the water to be regarded with disfavor.
4	Decided.	An odor that would force itself upon the attention that might make the water unpalatable.
5	Very Strong.	An odor of such intensity that the water would be absolutely unfit to drink. A term to be used only in extreme cases.

**Taste.** May be made on hot and cold samples. A simple statement following largely the terms applied to odor in expressing results, brackish, astringent, salty, sweetish, etc.

<sup>1</sup> Care should be taken that this be the bright yellow platonic salt, and not contaminated with the reddish platinous salt.

<sup>2</sup> App. made by Builders' Iron Foundry, Providence, R. I.

## CHEMICAL TESTS

## Free Ammonia

**Apparatus.** The apparatus for this determination should be as far as possible free from joints or connections that are subject in any way to outside

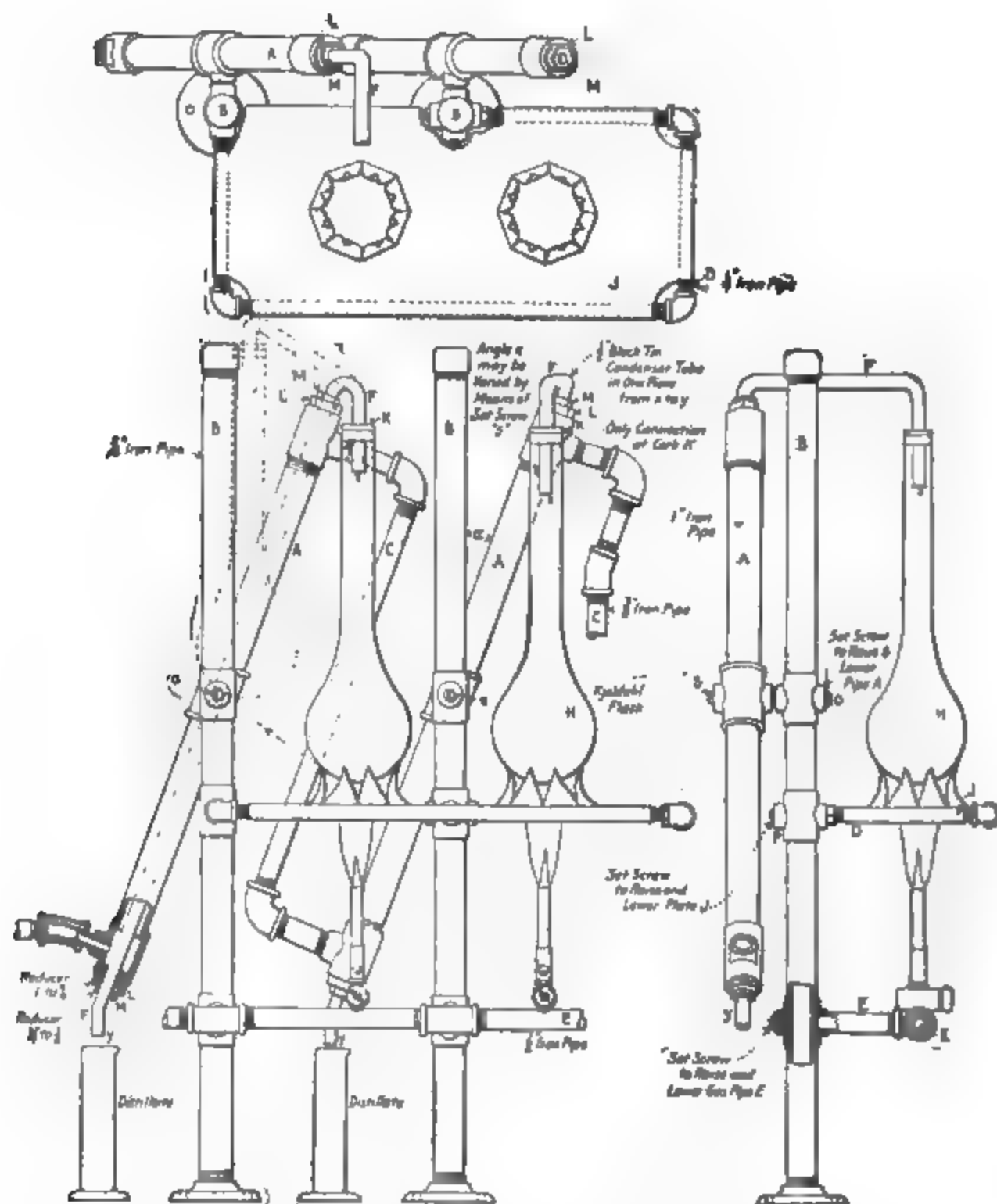


FIG. 171.

contamination or to decomposition. The apparatus is composed of a distillate flask and a condenser, with possibly a safety tube located somewhere near the flask to avoid the possible carrying over of impurities in connection with the steam.

**Reagents.** 1. *Ammonia-free Water.*

2. *Standard Ammonium Chloride Solution.* Dissolve 3.82 grams of ammonium chloride in 1 liter of distilled water. Dilute 10 cc. of this to 1 liter with ammonia-free water. 1 cc. = 0.00001 gram of nitrogen.

3. *Nessler's Solution.* Dissolve 50 grams of potassium iodide in the smallest possible quantity of cold water. Add a saturated solution of mercuric chloride until a faint show of excess is indicated. Add 400 cc. of 50% solution of potassium hydrate. After same has clarified by sedimentation, make up to 1 liter with water, allow to settle and decant.

**Optional Method.** Dissolve 61.75 grams of potassium iodide in 250 cc. of re-distilled water, and add a cold solution of mercuric chloride which has been saturated by boiling with excess of salt. Pour in the mercury solution cautiously, and add an amount just sufficient to make the color a permanent bright red. With a little practice the exact depth of color can be easily duplicated. It will take a little over 400 cc. of the mercuric chloride solution to reach this end-point. Dissolve the red precipitate by adding exactly .75 gram of potassium iodide. Then add 150 grams of potassium hydrate dissolved in 250 cc. of water. Make up to 1 liter. Mix thoroughly and allow the precipitate formed to settle. Pour off the supernatant liquid. Mercuric chloride increases the sensitiveness and potassium iodide decreases it.

**Operation.** Clean apparatus thoroughly as follows:

Fill a flask, which for most satisfactory results should be an 800-cc. Kjeldahl flask, with 500 cc. of distilled water. Add a pinch of c.p. sodium carbonate and distill first of all with no running water in the condenser jacket until free steam blows through the apparatus. Then turn on condenser water and distill off approximately 250 cc., testing the last 50 cc. with Nessler's solution, and this portion should not show color in fifteen minutes' time. The flask is then emptied of the remaining water, 500 cc. of the water to be analyzed placed therein, and if acid, neutralized with c.p. sodium carbonate. A slight excess hurries the ammonia liberation but also tends to cause bumping. The distillation is then started, distilling 6 cc. to 10 cc. per minute, and three separate portions of 50 cc. each are caught in Nessler jars. After 150 cc. is distilled the flame should be removed. To each 50-cc. portion add 2 cc. Nessler's solution and after ten minutes' standing compare with standards from the standard ammonium chloride solution.

### Albuminoid Ammonia

**Reagent.** 1. *Alkaline Potassium Permanganate.* Dissolve 200 grams of potassium hydrate and 8 grams c.p. potassium permanganate in 1250 cc. of water, boil down to 1 liter and bottle while still warm.

**Operation.** Add 50 cc. alkaline potassium permanganate solution and several pieces of washed and ignited pumice to the water remaining in the flask from the free ammonia determination and continue the distillation, taking off four or five separate portions of 50 cc. each in Nessler jars. Add 2 cc. Nessler's solution to each and after ten minutes standing compare color with standard as in the free ammonia determination.

### Organic Nitrogen

While this determination is not usually made we give it for the sake of completeness.

The portion of sample from the free ammonia determination, or a new portion freed from free ammonia by distillation, is acidified with 5 cc. C.P. sulphuric

acid (nitrogen-free) and digested in a hood until colorless and  $\text{H}_2\text{SO}_4$  fumes are given off. A little ignited pumice will guard against bumping. Remove from flame, add potassium permanganate in small portions until a heavy greenish precipitate persists, cool, dilute with ammonia-free water, neutralize with 10%  $\text{Na}_2\text{CO}_3$  solution ( $\text{NH}_3$  free), distill into Nessler tubes and compare as in free and albuminoid ammonia.

*Permanent standards*<sup>1</sup> can be made using potassium platonic chloride, 2 grams dissolved in water, 100 cc. strong hydrochloric acid and made to 1 liter; and cobalt solution, 12 grams cobaltous chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) dissolved in distilled water, 100 cc. strong hydrochloric acid added and made to 1 liter. The following table represents the amounts used, to be made to 50 cc. with distilled water in Nessler tubes for comparison, the 150-cc. mark being 20–25 cm. above the bottom, but should be checked against Nesslerized standards and the Nessler solution modified, if necessary, until the standards agree. This is accomplished by varying the amounts of potassium iodide and mercuric chloride.

Equivalent Volume of Standard Ammonium Chloride, cc.	Platinum Solution, cc.	Cobalt Solution, cc.
0.0	1.2	0.0
0.1	1.8	0.0
0.2	2.8	0.0
0.4	4.7	0.1
0.7	5.9	0.2
1.0	7.7	0.5
1.4	9.9	1.1
1.7	11.4	1.7
2.0	12.7	2.2
2.5	15.0	3.3
3.0	17.3	4.5
3.5	19.0	5.7
4.0	19.7	7.1
4.5	19.9	8.7
5.0	20.0	10.4
6.0	20.0	15.0
7.0	20.0	22.0

### Nitrogen as Nitrite

**Reagent.** 1. *Sulphanilic Acid.* Dissolve 8 grams of the acid in 1 liter of acetic acid, specific gravity 1.04. This is practically a saturated solution and keeps well.

2. *Naphthylamine Acetate.* Dissolve 5 grams of  $\alpha$ -naphthylamine in 1 liter of acetic acid, specific gravity 1.04, and filter through absorbent cotton (previously washed).

**NOTE.** A slightly pink color resulting on standing does not materially interfere with the use of this solution.

3. *Sodium Nitrite Solution.* Dissolve 1.1 grams of silver nitrite in nitrite-free water. Precipitate the silver with sodium or potassium chloride solution and dilute

<sup>1</sup> Permanent Standards (Jackson, Tech. Quart., 1900, vol. 13, p. 320.)

to 1 liter. Dilute 100 cc. of this solution to 1 liter and then 10 cc. of this second solution to 1 liter with sterilized nitrite-free water, adding 1 cc. of chloroform and holding in a sterilized bottle. 1 cc. = 0.0001 milligram of nitrogen.

**Operation.** Take 100 cc. of the water after filtration and clarification, preferably with aluminum hydrate, to remove possible suspended iron and material which might interfere with color production. Add 2 cc. each of solutions No. 1 and No. 2. After ten minutes' standing compare with standards made up from the standard sodium nitrite solution (No. 3).

### Permanent Standards

**Cobalt Solution.** Dissolve 24 grams of cobaltous chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) in distilled water, add 100 cc. of strong hydrochloric acid and make up to one liter with distilled water.

**Copper Solution.** Dissolve 12 grams of dry cupric chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) in distilled water, add 100 cc. of strong hydrochloric acid and make up to one liter with distilled water.

The standards are used in 100-cc. tubes with the mark 12-14 cm. above the bottom. The following table gives the proportions of each solution to be made up to 100 cc.:

cc. Cobalt Solution.	cc. Copper Solution.	p.p.m. Nitrite per 100 cc. of Water.
.0	.0	0.000
1.1	1.1	.001
3.5	3.0	.003
6.0	5.0	.005
12.5	8.0	.010

The solutions to use for 100 cc. of water are the old ones, as follows: 1 cc. of hydrochloric acid (1 : 4), 2 cc. of sulphanilic acid (8 grams per liter), and finally 2 cc. of naphthylamine hydrochloride (8 grams per liter with 10 cc. of strong hydrochloric acid), and allow color to develop twenty minutes.

**NOTE.** Volume 28, page 742, J. Soc. Chem. Ind., calls attention to the possibility of a permanent standard composed of a solution of acid magenta (fuchsin-S, acid fuchsin according to Weigert). According to this article, 0.2 of a gram of this dye is dissolved in 50 cc. of 2/N HCl and made up to 2000 cc. with distilled water. Of this solution 200 cc. are mixed with 50 cc. of 2/N HCl and again diluted to 2000 cc. with distilled water. From this latter solution standard solutions can be prepared containing various quantities, these standards being made up to 200 cc. with distilled water after the addition of 5 cc. of 2/N HCl. Considerable work is being done on this, but the standards have not yet been accepted in this country. However, standards can be made by matching these solutions against standards prepared in the usual way and their permanence is much greater than such standards.

## Nitrogen as Nitrate

### Phenolsulphonic Acid Method

**Reagent. 1. Phenolsulphonic Acid.** Dissolve 25 grams of pure white phenol in 150 cc. of pure concentrated sulphuric acid, add 75 cc. of fuming sulphuric acid (15%  $\text{SO}_3$ ), stir well and heat for two hours at about  $100^\circ$ .<sup>1</sup>

<sup>1</sup> Jour. Amer. Chem. Soc., 33, 382, 1911.



2. *Ammonium Hydrate* 1-1.

3. *Sodium Carbonate*. 10% solution of anhydrous  $\text{Na}_2\text{CO}_3$ .

4. *Standard Nitrate Solution*. Dissolve 0.72 gram pure or C. P. potassium nitrate in 1 liter of distilled water. Evaporate carefully 10 cc. of this solution on water bath, moisten thoroughly with 2 cc. of solution No. 1 and dilute to 1 liter. 1 cc. of this = 0.001 milligram of nitrogen.

**Determination.** Carefully evaporate 100 cc. of water after the addition of 2 cc. of sodium carbonate solution. After this evaporate to dryness, cool and add 2 cc. phenolsulphonic acid (No. 1), mixing well with a glass rod. Dilute with 25 cc. of distilled water and add an excess of ammonium hydrate, making up to 100 cc. volume with distilled water.

The dilute solution is then compared with the standard solution.

**Notes.** When the chlorides are over 100 parts per million in the original sample they should be removed with the addition of silver sulphate in the solid form and the water should be filtered prior to evaporation. It is for this reason that ammonium hydrate is used to develop the color instead of potassium hydrate, which is frequently recommended, as a slight excess of silver sulphate will result in a dirty precipitate when using potassium hydrate, whereas the use of ammonia has no effect. Furthermore, the filtration of a turbid nitrate solution does not result in a satisfactory color, as would be the case without filtration.

*Permanent standards* can be made by procedure given on page 539, or standards can be made using tripotassium nitrophenoldisulphonate. The following method is given in an article in the J. Amer. Chem. Soc., Vol. 33, pp. 381-384:

The theoretical amount of powdered potassium nitrate is added to the disulphonic acid reagent in small pinches at a time (for each cc. of reagent 0.1076 gram  $\text{KNO}_3$ ), stirring thoroughly after each addition. The product is then diluted, treated with dry barium carbonate to a deep yellow color, filtered and the precipitate washed with boiling water to remove the barium salt which is but slightly soluble in cold water. This extraction must be thorough. Filtrate and washings are united, the barium removed by the addition of potassium carbonate until alkaline, the solution filtered and the filtrate concentrated and crystallized. The solution may then be easily purified by crystallization. In preparing the standards, however, solutions made from known amounts of nitrate standards will match up with this recrystallized solution, and by means of proper dilutions the series of standards can be made. Standards made this way will last for many months, whereas standards made from the standard nitrate solution are apt to lose value in a month's period and should be made up very frequently.

#### Optional Method—Aluminum Reduction<sup>1</sup>

**Reagents.** 1. *Sodium or Potassium Hydrate Solution*. Dissolve 250 grams of the hydrate in 1250 cc. of distilled water, add several strips of aluminum foil and allow action to pass overnight. Boil down to 1 liter.

2. *Aluminum Foil*. Use strips of pure aluminum approximately 10 cm. long, 9 mm. wide, and  $\frac{1}{8}$  mm. thick, same to weigh about  $\frac{1}{8}$  gram.

**Operation.** 100 cc. of water is placed in a 300-cc. casserole. Add 2 cc. of the hydrate solution and boil down to about 20 cc. Pour the contents of the casserole into a test-tube about 6 cm. long and 3 cm. in diameter and of approximately 100-cc. capacity. Rinse the casserole several times with nitrogen-free water and add the rinse water to that already in the tube, thus making the contents of the tube approximately 75 cc. Add a strip of aluminum foil. Close the tube by means of a rubber stopper through which passes a  $\Lambda$ -shaped glass tube about 5 mm. in diameter. Make the short end of the tube flush with the lower side of the

<sup>1</sup> Univ. of Illinois Bull. Water Survey, Series 7, p. 14, 1909; Amer. Jour. Public Hygiene, 19, 536, 1909.

rubber stopper while the other end extends below the surface of distilled water contained in another test-tube. This apparatus serves as a trap through which the evolved hydrogen escapes freely. The amount of ammonia escaping into the trap is slight and may be neglected. Allow the action to proceed for a minimum period of four hours, or overnight. Pour contents of the tube into a distilling flask, dilute with 250 cc. of ammonia-free water, distill and collect in Nessler tubes and Nesslerize. When the nitrate content is high, collect the distillate in a 200-cc. flask and Nesslerize an aliquot portion. If the supernatant liquid in the reduction tube is clear and colorless, the solution may be diluted to a definite volume and an aliquot part Nesslerized without distillation.

**NOTE.** Where the nitrates are very high, from 50 parts per million up, note additional method given under the head of Nitrate Determination in Mineral Analysis of Water.

### Oxygen Consumed

**Reagents.** 1. *Standard Potassium Permanganate Solution.* Dissolve 0.4 gram C.P. salt in 1 liter of distilled water. 1 cc. is equivalent to 0.1 milligram available oxygen.

2. *Standard Ammonium Oxalate Solution.* Dissolve 0.888 gram C.P. ammonium oxalate in 1 liter of distilled water. 1 cc. is equivalent to 0.1 milligram of oxygen. The standard permanganate solution must be standardized against the ammonium oxalate solution.

3. *Dilute Sulphuric Acid 1-3.*

**Operation.** 100 cc. of water are measured into a 450-cc. Erlenmeyer flask, acidified with 5 cc. dilute sulphuric acid. Ten cc. of standard permanganate solution is run in from a burette and the flask is placed in a bath of boiling water, the level of which is above the level of the flask contents, for thirty minutes. Remove. Add 10 cc. of standard oxalic solution and then determine the excess with the standard permanganate solution. Deduct from the total permanganate solution used the 10 cc. of oxalic acid, and the remainder represents oxygen consumed. For particularly bad waters smaller quantities of the sample are taken and diluted to 100 cc., as it is undesirable at any time in the course of boiling that the pink color of permanganate be completely discharged.

### Chlorine as Chlorides

**Reagents.** *Standard Salt Solution.* 16.48 grams fused C.P. sodium chloride are dissolved in 1 liter of distilled water. 100 cc. of this solution diluted to 1 liter gives a standard solution, each cc. of which contains .001 gram of chlorine.

*Standard Silver Nitrate Solution.* 4.8 grams dried silver nitrate crystals are dissolved in one liter of distilled water. Each cc. of this solution is equivalent to approximately .001 gram of chlorine, standardized against the Standard Salt Solution.

**NOTE.** N/50 solutions of both sodium chloride and silver nitrate can be used where it is inconvenient to make too many standard solutions, using the proper factors.

*Potassium Chromate.* Ten per cent solution neutral potassium chromate.

**NOTE.** A. P. H. A., page 43, recommends 5 per cent solution of neutral potassium chromate, adding after solution of the crystals in a few cc. of water, sufficient silver nitrate to produce a slight red precipitation. This is filtered off, and the filtrate made up to volume.

**Operation.** 100 cc. of the sample are titrated with silver nitrate solution, using 1 cc. of the potassium chromate as indicator to the first persistence of the silver chromate red. Subtract 0.2 cc. blank from the reading. A white porcelain dish or casserole is the preferable container, although a flint-glass beaker over a white porcelain plate may be used. Where a chlorine is high and more than 15 cc. of silver nitrate is used, a smaller sample (50 cc. or 25 cc.) should be taken and distilled water added to bring the volume up to approximately 100 cc. If the original water is noticeably colored, 25 to 30 by standard, it may be decolorized by adding precipitated aluminum hydrate, bringing to a boil and filtering. Titration must always be made in the cold, however.

**NOTE.** Precipitated aluminum hydrate is prepared by dissolving potash alum in water, precipitating by adding carefully ammonia and washing in a large jar with distilled water, by decantation, until free from chlorine, ammonia, and nitrites. An acid water should first be neutralized with sodium carbonate and a water containing free hydrates should be neutralized with sulphuric acid. Where specially accurate work is desired, observations may be made in a dark room with a yellow light. (A. P. H. A., page 44.) A yellow photographic glass may be used in daylight and at night the ordinary carbon filament electric light.

### Total Solid Residue

Evaporate 50 cc. to dryness, in a platinum dish, at about 270° Fahr., and bake for at least 30 minutes at that temperature. An ordinary water-bath temperature will not remove water of crystallization from alkali sulphates or calcium sulphate. Where water is high in magnesium salts, as determined in mineral analysis, the water-bath temperature is more satisfactory, due to the readiness with which magnesium chloride and frequently magnesium carbonate will decompose to oxide. As a rule, however, a temperature from 240° to 270° meets most of the conditions.

Weight to tenths of milligram times 1168 = grs. per gal. total solids.

Weight to tenths of milligram times 20,000 = parts per million total solids.

Residues from acid waters should be ignited to a dull red heat after addition of a drop or so of sulphuric acid, to insure complete removal of the acid itself, which will not go off at the temperature stated. This will result in the decomposition of all iron compounds to the oxide form, and will fix all salts, lime, magnesium, sodium and potassium, in the sulphate form, and correction should be made for chlorides present, which would be converted into sulphate.

Waters high in magnesium salts should be evaporated at the first specified temperature, adding, however, a few cc. of 50 normal sodium carbonate solution to insure a slight excess of sodium carbonate, correcting for the weight of sodium carbonate added. Where the waters contain much organic matter after weighing, they may be very gently ignited at a very dull red heat until the carbon has been burned off. After cooling, the residue may be recarbonated with tested ammonia carbonate solution, and again dried in the usual way. The difference in weight after titrating for possible loss of chlorides, due to volatilization, gives a close approximation of the organic matter present. Similarly, waters high in magnesium chloride or nitrate compounds may be evaporated with a few drops excess of sulphuric acid, and ignited to a dull red heat, the residue being compared, where a complete analysis is made, with the sum of all bases calculated to the sulphate form. This is sometimes more convenient and satisfactory than the evaporation with excess sodium carbonate.

## INTERPRETATION OF RESULTS

The interpretation of the results of a sanitary water analysis is largely a matter of experience, and it is impossible to lay down hard and fast rules covering this one matter. It is, however, possible to sum up the meanings of the various determinations made, as each determination has some bearing upon the sanitary condition.

In physical data the turbidity refers to insoluble matter in suspension. In many cases it is perfectly harmless, although less attractive, and frequently suggests contamination, which is as apt to be present as not. High turbidities, following rain storms or lake over-turnings, are usually accompanied by *B. coli*, the intestinal organism, in considerable quantity. The turbid waters of the West may cause stomach trouble until a person is accustomed to them. Color is due, usually, to an extract of vegetable or organic matter, or to iron salts, and in itself has no value save suggesting organic contamination. Highly colored water may have an astringent taste, and is not looked upon with favor by the consumer. It may cause corrosion in pipes and boilers.

Various organic matters are in no way determined in this analysis, the results obtained being simply indications of certain cycles in decomposition of nitrogenous material, as no decomposition can take place without some resulting nitrogen compound. Free ammonia represents the first stage in this decomposition, and represents the amount of organic matter present in a partially decomposed and decomposing state. Deep wells in glacial drift frequently also contain high ammonia, however, which would in no way suggest active contamination.

Albuminoid ammonia represents organic substances in an undecomposed state, which will, however, decompose under the proper conditions. The presence of nitrogen in such combination in large amount usually suggests the presence of pollution of a sewage character. However, its presence usually accompanies and varies in amount with the color and with the microscopic organisms.

The next stage in the cycle is nitrogen as nitrites, indicating that decomposition is actively progressing. Nitrite in surface water may indicate contamination when in considerable quantity, but in ground water is absolutely of no significance. (Proc. Am. W. W. Assoc., 1908, page 323.) Its presence is due to the action of certain types of bacteria either as a product of oxidation from free ammonia or as a product of reduction from nitrate. Ferrous compounds have also a bearing on such reduction.

The final state of decomposition is nitrogen as nitrate. This indicates the fact that at some time in the past organic matter has been present. Its presence indicates a purified water. In large amounts it may cause itching in sensitive persons. It is an important cause of corrosion in pipes and boilers.

The oxygen consumed represents the amount of oxygen required to oxidize organic matter already in the water. It has a bearing upon the organic matter, but there are many inorganic substances which also discharge the color of the permanganate solution, and the result should always be considered in the presence of the other determinations.

Chlorine as chlorides, if above the normal figure for any definite location, is a fairly good indication of sewage, as it is one of the most constant and principal constituents of sewage.

The total residue itself should not be too high, as an excess of inorganic

materials would stamp the water unfit from an industrial point of view, and also, from the standpoint of the individual, might make it unsatisfactory as a drinking supply, for daily consumption.

With reference to standards of purity, it is impossible to make absolute standards. We quote as a matter of interest a table published by the State of Illinois, giving their suggested limits of impurities for supplies in that State. (The remarks which follow are those of the State Geological Survey.)

	Lake Michigan.	Streams.	Springs and Shallow Wells.	Deep Drift Wells.	Deep Rock Wells.
Turbidity.....	None	10.	None	None	None
Color.....	None	.2*	None	None	None
Odor.....	None	None	None	None	None
Residue on Evaporation...	150.	100	500.	500.	100
Chlorine.....	4.5	6.	15.	15.	5.-100
Oxygen consumed.....	1.6	5.	2.	2.-5	2.-5
Nitrogen as:					
Free Ammonia.....	.01	.05	.02	.02-3	.02-3
Albuminoid Ammonia..	.08	.15	.05	.20	.15
Nitrites.....	.000	.000	.000	.000	.000
Nitrates.....	.04	.5	2.00	.50	.5
Alkalinity.....	120.	200	300.	300.	300.
Bacteria per cc.....	100.	100	100	100.	100.
Colon bacillus in one cc...	Absent	Absent	Absent	Absent	Absent

\*Modified Nessler or Natural Water Standard equal 26 p.p.m. platinum scale.

The formation of a reasonable and just opinion regarding the wholesomeness of a water requires that there be taken into consideration all the data of the analysis, together with the history of the water; the nature of the source; character of the soil and earth or rock strata, and the surroundings. The interpretation of results is a task for the expert.

Chlorine is the most permanent element shown in water analysis, as it is never removed from water by any changes or processes of purification. Salt deposits, however, in the soil must also be taken into consideration.

## MINERAL ANALYSIS

## Outline of Procedure

- 50 cc. (Certified pipette or burette) evaporated to dryness at 270° F. in weighed platinum dish. Increased weight of dish represents *total solid residue*. (Can be used for  $\text{SO}_4$  when sample is small.) Ignite for organic loss.
- 250 cc. Titrate with N/10 acid or alkali for *alkalinity or acidity*. (Can be re-used to make up volume of 500-cc. portion when water sample is small.) Methyl orange indicator.
- 100 cc. Titrate with N/10  $\text{AgNO}_3$  for *chlorine*.
- 100 cc. Acidify, boil, precipitate with  $\text{BaCl}_2$ , filter and weigh for *total sulphate*. (Use filtrate for Na and K when necessary.)
- 100 cc. Add 2 cc. 10%  $\text{Na}_2\text{CO}_3$ , evaporate to dryness, add phenolsulphonic acid, dilute, then excess of  $\text{NH}_4\text{OH}$  for *total nitrate*.
- 500 cc. Evaporate to dryness (with a few cc. concentrated  $\text{HCl}$  when very accurate  $\text{SiO}_2$  figure is necessary) in No. 8 R. B. dish. Bake 30 minutes, cool, add boiling  $\text{HCl}$  (concentrated), dilute and filter.

Precipitate is $\text{SiO}_2$ and silicate impurities (also $\text{BaSO}_4$ ). Unless great accuracy is necessary, it should be weighed as such, otherwise $\text{SiO}_2$ can be removed by $\text{HFl}$ and correction made.	Filtrate. Add a few drops of $\text{HNO}_3$ , concentrate to 50 cc., cool, add $\text{NH}_4\text{OH}$ , boil and filter.	
	Precipitate (Fe, Al, Phos.) may be reported as such or as Fe and Al after Qual. test for phosphate has shown same to be absent. Otherwise both Fe and Phos should be determined and weight corrected.	Filtrate. Boil and add saturated Am. Oxalate drop by drop, boil and filter.
	Prec. Ca as oxalate, dry, ignite and weigh as $\text{CaCO}_3$ or $\text{CaO}$ .	Filtrate Mg (and Mn) add 50 cc. concentrated Sod. Phos. Solution, then 50 cc. $\text{NH}_4\text{OH}$ , stir well 2 minutes, or more, let stand 4 hours, or more, filter and wash with 3% $\text{NH}_4\text{OH}$ . Ignite and weigh (determine Mn separately and correct when necessary).

NOTE. For industrial purposes the original addition of  $\text{HCl}$  is not always necessary and correction for  $\text{BaSO}_4$ , Phos. Mn and separation of Fe and Al can be dispensed with unless there is cause to suspect one to be present in material amounts.

In the matter of mineral analysis of water, it is not so hard to obtain a complete analysis of the water, including the non-incrusting or "nearly always" soluble materials as well as the incrusting materials, as it is to make numberless individual or independent tests, in the hope of drawing conclusions from same. The scheme of analysis which follows is used exclusively in the writer's laboratories, and when carried out as given, makes it possible to complete analysis of a water, or a group of waters numbering up to ten, in the period of eight hours elapsed time, or twenty-four hours, assuming the work is arranged in such a way that the magnesia precipitates are allowed to stand overnight before filtration. On another page will be found a skeleton form for this complete analysis, and this skeleton will serve as a rough guide to the more extended discussion which will follow.

The complete analysis considers the quantitative determinations of silica, iron and aluminum, calcium, magnesium, sodium and potassium, as bases, and carbonate, hydrate, nitrate, sulphate, chloride, and phosphate, as radicals or acids, with suggested methods for manganese, ammonia, barium, and other materials which might possibly be present.

Prior to the starting of the analysis, the physical characteristics of the water should be noted, turbid waters should be filtered, the suspended matter analyzed separately when necessary, and the amount determined either by filtration and weighing of the separated material (alundum cones are very satisfactory), or by the difference between two residues, one of which represents the original water and one the filtered water. The mineral analysis should represent the filtered supply. This is due to the difficulty of getting uniform samples with suspended matter at different times.

### Silica, Iron, Aluminum, Calcium, Magnesium

#### (Manganese, Phosphoric Acid)

**NOTE.** If from qualitative observations the water contains considerable mineral matter, smaller quantities varying from 100 to 250 cc. may be taken, or if the sample is apparently distilled or condensed and contains very little mineral matter, 1000 cc. should be taken, the object being to obtain a residue neither too large nor too small. 0.4 to 0.6 gram is a good quantity to work on.

#### Silica

Evaporate over free flame, then on  $\frac{1}{4}$ -in. asbestos board, to dryness, 500 cc. original water, using a No. 8 porcelain dish. Bake at 110–130° C. or on asbestos plate over flame for one-half hour. Moisten with 10 cc. concentrated HCl, add 50 cc. of water, boil fifteen to thirty seconds and filter. Wash with hot water.

**NOTE.** For great accuracy, evaporate twice to dryness as above, with the addition, prior to the sample going to dryness, of 10 cc. HCl, allow to bake as above, following from there on the usual procedure for filtration.

The precipitate retained on the filter paper represents the silica or siliceous matter, including possibly barium sulphate. Ignite and weigh.

**NOTE.** If the amount is over .01 gm. per liter, or 8 parts per million, moisten with a few drops of concentrated sulphuric acid and hydrofluoric acid, expel excess acids, and reweigh. This must be done in platinum. The loss represents silica, and should

be recorded as such, and the residue represents bases, principally barium, combined with sulphuric acid. This will also catch possible calcium sulphate that might be left undissolved, due to short boiling, to low dilution, or conditions which would prevent its normal solubility in the original solution.

### Iron and Aluminum (Gravimetric)

The filtrate contains iron, aluminum, calcium, magnesium, possibly manganese, and phosphate. Bring to a boil, add two or three drops conc. nitric acid and concentrate to about 25 cc. Remove from hot plate or flame, add ammonium hydroxide in slight excess, boil for one or two minutes, and filter.

The precipitate contains iron, aluminum, and possibly phosphates. Burn and weigh as oxides of iron and aluminum, plus phosphates, and test 50 cc. of the original water with treatment in the usual way to determine whether or not phosphates are present. Where this precipitate of iron and aluminum oxides is greater than 0.01 gm. per liter or 8 parts per million, or where the separation of the iron and aluminum is advisable, the precipitate should be fused with eight or ten times its weight of potassium bisulphate, redissolved in water, the iron reduced to the ferrous condition with zinc, and titrated with potassium permanganate, recording the difference in weight between the original precipitate and the iron determination as aluminum oxide.

$$\text{Fe} \times 1.43 = \text{Fe}_2\text{O}_3$$

**NOTE.** Where much water is available and time is an object, an additional 500 cc. can be carried down to approximately 50 cc. with a few drops of nitric acid, the iron and aluminum precipitated as above mentioned with ammonia, and the precipitate before drying redissolved in acid, reduced and titrated with potassium permanganate. This portion can be started at the same time the original analysis is started, and will greatly simplify the determination and save time.

### Total Iron (Colorimetric)

**Reagents. Iron Standard.** 0.7 gm. cryst. ferrous ammonium sulphate is dissolved in a small amount of distilled water, add 25 cc. dilute (1-5) sulphuric acid, warm slightly and oxidize completely with potassium permanganate, make up to 1000 cc. 1 cc. = 0.1 mg. Fe.

**Potassium Sulphocyanide.** 2 per cent solution.

**Potassium Permanganate.** 6.3 gms. per liter.

**Operation.** Instead of precipitating, or where *traces* of Fe are of importance, 100 cc. to 1000 cc. of the water may be carried to dryness with HCl and a few drops of Br, taken up with 5 cc. (1 : 1) HCl, diluted to 100 cc. in a Nessler tube, 10 cc. KCNS solution (20 gms. to a liter) added and the color compared with standards. The comparison should be made at once as the color fades.

**NOTE.** It is frequently as satisfactory to add the standard iron solution from a burette to a 100 cc. Nessler tube containing 5 cc. (1 : 1) hydrochloric acid (Fe free), 10 cc. potassium sulphocyanide solution (20 gms. to a liter) and sufficient distilled water until the color matches that of the sample.

### (Ferrous Iron—Colorimetric)

(Frequently desirable in acid waters but rarely necessary.)

**Reagents. Iron Standard.** 0.7 gm. cryst. ferrous ammonium sulphate is dissolved in one liter of distilled water containing 10 cc. dilute  $\text{H}_2\text{SO}_4$ . (Not permanent. Should be made up as needed.) 1 cc. = 0.1 mg. Fe.



**Potassium Ferricyanide Solution.** (Prepare as needed.) 0.5 g. per 100 cc. distilled water.

**Sulphuric Acid.** 1 : 5.

**NOTE.** Prepare sample and standards at same time.

**Operation.** Place in 100 cc. Nessler jar 50 cc. of sample, 10 cc. dilute  $H_2SO_4$  (1-5), filter, if necessary, to remove suspended matter, add 15 cc. potassium ferricyanide solution and make up to 100 cc. mark with distilled water. Compare with standards made as follows:

Place in 100 cc. Nessler jar 75 cc. distilled water, 10 cc. dilute  $H_2SO_4$  (1-5) and 15 cc. potassium ferricyanide solution, and mix well. Add various amounts of iron standard from burette, mix and compare color. Determine ferric iron by deduction of ferrous iron from total iron.

### Phosphates

**Reagents. Ammonium Molybdate.** 50 gms. c.p. neutral salt dissolved in 1 liter distilled water.

**Nitric Acid** (spec. grav. 1.07). Dilute about 1-5 with distilled water.

**Standard Phosphate Solution.** 0.5324 gm. c.p. cryst.  $Na_2HPO_4 \cdot 12H_2O$ . Dissolve in distilled water, 100 cc. standard  $HNO_3$  added. Dilute to 1 liter.

One cc. = 0.0001 gram  $P_2O_5$ .

**Operation.** Evaporate 50 cc. water to dryness in porcelain after addition of 3 cc.  $HNO_3$  (spec. grav. 1.07). Bake two hours at  $212^\circ F$ . Take up with 50 cc. distilled water, add 4 cc. molybdate solution and 2 cc.  $HNO_3$ , and compare in Nessler tube with standards from phosphate solution made to 50 cc. and treated with same reagents. A tube 2.5 cm. by 24 cm. to 100-cc. mark of hard, white glass is most suitable.<sup>1</sup> Where waters are already colored the evaporation should be carried on with 3 cc.  $HNO_3$  and 0.5 cc. (or more, if water is highly colored) of  $KMnO_4$  solution, (1 gram per 1000 cc.), baking at  $212^\circ F$ . for the same time.<sup>2</sup> Where the phosphate is present in large enough quantities to precipitate the gravimetric methods may be used.

### Calcium

The filtrate from iron, aluminum and phosphate precipitate contains calcium, magnesium, and possibly manganese. Concentrate to about 100 cc. Add to the hot ammoniacal solution a concentrated (saturated) solution of ammonium oxalate drop by drop, or add in small portions crystals of ammonium oxalate. Allow to boil two minutes, stirring, if necessary (on account of heavy precipitate and tendency to bump), remove, filter and wash. (Five complete washings are usually sufficient.)

**NOTE.** Where great accuracy is desired, the precipitate on the filter should be redissolved in a small amount of hot, dilute, hydrochloric acid and reprecipitated with ammonium oxalate.

The calcium oxalate upon the filter paper can now be burned and weighed either as calcium oxide or calcium carbonate.

<sup>1</sup> J. Am. Chem. Soc., 23, 96, 1901.

<sup>2</sup> J. Ind. and Eng. Chem., 5, 301-2, 1913.

**NOTE.** The burning of calcium oxalate to carbonate is not so difficult as it seems, as an intense heat is necessary to convert it to the oxide, and if the crucible is well watched and the flame gives just sufficient heat to carbonize and destroy the filter paper, there will be no chance whatever of any calcium oxide being formed, or any calcium oxalate being left. Where hypothetical combinations are used, it is very convenient to have the calcium as carbonate without calculation. Where burned to the complete oxide it is frequently necessary to use a blast lamp, as large precipitates require a high temperature to reduce completely to oxide form.

#### Optional (Volumetric)

Or it may be dissolved in 2% sulphuric acid and titrated with the standard solution of potassium permanganate. (N/50  $\text{KMnO}_4$  may be used.)

**NOTE.** Where the volumetric method is to be used, five complete washings are not, as a rule, sufficient, as the presence of traces of ammonia salts, while not interfering in any way with the gravimetric determination, are prone to have considerable influence upon the volumetric results, due to the possibility of traces of ammonium oxalate still being present.

$$\text{Fe Value} \times 0.895 = \text{CaCO}_3.$$

$$\text{Fe Value} \times 0.5016 = \text{CaO}.$$

$$\text{Fe Value} \times 0.3584 = \text{Ca}.$$

#### Magnesium

*The filtrate contains magnesium (and possibly manganese).* Acidify with  $\text{HCl}$ , concentrate, if necessary, to 150 cc., add 25 cc. saturated solution of ammonium sodium hydrogen phosphate ( $\text{NH}_4\text{NaHPO}_4 \cdot 4\text{H}_2\text{O}$ , microcosmic salt), cool and make alkaline with ammonium hydrate. Allow to stand at least four hours, filter and wash with 3% solution of ammonium hydrate. Burn and weigh as  $\text{Mg}_2\text{P}_2\text{O}_7$ .

**NOTE.** Accurate results are also obtained with the use of sodium phosphate added direct to the filtrate from the calcium precipitate without previously acidifying with acid, with 25 cc. to 50 cc. of ammonium hydrate added to make strongly alkaline, after which the solution should be very thoroughly stirred (for at least two minutes), using a rubber-ended glass rod. Allow to stand at least four hours.

For very rapid work in either case, if the magnesium solution after the precipitation is cooled in ice-water, filtration can be frequently made in two hours' time.

For extremely accurate work the precipitate produced in either of the methods above should be redissolved in a little dilute  $\text{HCl}$  and the precipitation repeated.

#### Optional (Volumetric)

**Reagent.** *Sodium Arsenate*, 10% solution.

The filtrate from the calcium precipitate, or an original portion of 500 cc. from which iron, aluminum and calcium have been removed as above, is acidified. Concentrate to the point of crystallization, after which approximately one-third by volume of ammonium hydrate and 25 cc. sodium arsenate solution are added and the solution vigorously shaken for at least ten minutes, filtered, and the precipitate washed free from arsenic with distilled water to which has been added 3% C.P. ammonia water. Dissolve in 50 cc. dilute  $\text{H}_2\text{SO}_4$  (1:3), transfer to precipitation flask, dilute to approximately 100 cc. and add 3.4 grams potassium iodide. Allow to stand five minutes and titrate with standard thiosulphate solution until the yellow color of the liberated iodine just disappears. Starch as an indicator is not satisfactory, nor necessary. This method is not so accurate as the gravimetric method, giving slightly high results, but is good for rapid work.<sup>1</sup>

<sup>1</sup> J. Am. Chem. Soc., 29, 1464-7; *ibid*, 21, 146.

### Manganese

Where necessary, manganese should be determined separately in another portion of the water and corrections made. The Knorres Persulphate method is the most reliable for large amounts (10 milligrams Mn per liter); the Bismuthate method for smaller amounts.

#### Knorres, Persulphate Method (Volumetric)

**Reagents.** *Potassium Bisulphate* C. P.

*Ammonium Persulphate Solution* (60 grams per liter distilled water).

*Hydrogen Peroxide Solution.* Equivalent to N/10  $\text{KMnO}_4$ . (Approx. 5.6 cc. 3%  $\text{H}_2\text{O}_2$  diluted to 100 cc.)

**Operation.** Evaporate 5 liters or more to dryness, adding first 10 cc. concentrated  $\text{H}_2\text{SO}_4$ . Ignite after adding a few crystals of potassium bisulphate and take up in hot water. Transfer to 250-cc. Erlenmeyer flask with 5 cc. dilute (1 : 3)  $\text{H}_2\text{SO}_4$ , add 10 cc. ammonium persulphate solution, boil twenty minutes, cool, dissolve precipitate (manganese superoxide) in standard hydrogen peroxide solution. (If no ppt. forms no manganese is present.)

**Notes.** When hydrogen peroxide solution is standardized against N/10  $\text{KMnO}_4$ , 1 cc. will be equivalent to 2.754 milligram Mn.

An excess of 10–20 cc.  $\text{H}_2\text{O}_2$  Sol. can be added and this excess titrated with N/10  $\text{KMnO}_4$ .

#### Sodium Bismuthate Method (Colorimetric)<sup>1</sup>

**Reagents.** *Potassium Permanganate.* 0.288 gram  $\text{KMnO}_4$  to 1000 cc. 1 cc. = 0.1 milligram Mn.

*Sodium Bismuthate* (purest).

See method of preparation of reagent given on page 263.

**Nitric Acid.** (Spec. grav. 1.135) 3 parts concentrated  $\text{HNO}_3$  to 1 part  $\text{H}_2\text{O}$  should be blown with air until free from oxides of nitrogen.

**Sulphuric Acid.** 25 cc. concentrated  $\text{H}_2\text{SO}_4$  to 1000 cc. Add permanganate solution to a faint but noticeable color.

**Operation.** Evaporate 500 cc. in porcelain dish after adding 1 cc. dilute  $\text{H}_2\text{SO}_4$  in excess to that necessary to neutralize all alkali. Ignite to remove free acid (organic matter and chlorine), cool and dissolve in 50 cc.  $\text{HNO}_3$  (30 cc. concentrated  $\text{HNO}_3$  to 1 liter), with heat if necessary. Cool again, add 0.5 gram sodium bismuthate and heat until pink color disappears, re-cool and add sodium bismuthate in excess, filter through asbestos in Gooch crucible (asbestos must be free from organic matter, thoroughly washed and ignited), or alundum crucible. Wash with nitrite-free distilled water containing 5% dilute  $\text{HNO}_3$  (30 cc. concentrated  $\text{HNO}_3$  per liter), into Nessler tube, make up to 100 cc. and match with color produced by necessary amount of standard  $\text{KMnO}_4$  in 100 cc.  $\text{H}_2\text{SO}_4$  reagent.

No. cc. standard  $\text{KMnO}_4 \times 0.2$  = milligrams Mn per liter.

**Note.** The permanganate solution used for oxygen consumed (see Sanitary Method) contains 0.139 gram Mn per liter and may be used when necessary.

No. cc.  $\times 0.278$  = milligram Mn per liter.

<sup>1</sup> J. Am. Chem. Soc., 29, 1074–78, 1907.

### Sulphates

100 cc. of the water is slightly acidified with conc. HCl and 5 cc. 10 %  $\text{NH}_4\text{Cl}$  solution added, brought to a boil, and if turbid is filtered and washed four or five times with boiling water. The clear or original water is now brought to a boil and 10% barium chloride added drop by drop to the boiling solution in slight excess. Boil ten minutes, stirring from time to time, if the precipitate is heavy. Remove and allow to cool prior to filtering. The precipitate consists of barium sulphate. Wash free from chlorides, testing with  $\text{AgNO}_3$ . Dry, ignite and weigh.

$$\text{BaSO}_4 \times .411 = \text{SO}_4$$

$$\text{BaSO}_4 \times .583 = \text{CaSO}_4$$

$$\text{milligrams BaSO}_4 \times .338 = \text{CaSO}_4 \text{ grains per gallon.}$$

#### Benzidine Method. (Optional)<sup>1</sup>

**Reagents. Benzidine Solution.** Triturate in a mortar with 5 cc. to 10 cc. water, 4 grams benzidine base. Transfer to liter flask, add 10 cc. HCl and make to volume. 1 cc. = .0013 gram  $\text{SO}_4$ .

**Hydroxylamine Hydrochloride.** 1% solution in water.

**Operation.** Add 10 cc. hydroxylamine hydrochloride to 250 cc. water, then add, at once stirring well, 100 cc. benzidine solution. Allow to stand fifteen to twenty minutes, decant through vacuum filter and wash with 10 cc. to 20 cc. distilled water (do not let filter run dry), return filter paper to beaker, cover with distilled water, bring to a boil and titrate with N/10 or N/50 NaOH, using phenolphthalein as indicator.

$$\text{One cc. N/10 NaOH} = .0048 \text{ gram } \text{SO}_4$$

$$\text{One cc. N/50 NaOH} = .00096 \text{ gram } \text{SO}_4$$

**Note.** An accurate method by the turbidimeter is given by Hale in the chapter on Coal, page 675.

**N. B.** Method by Muer, Jour. Ind. Eng. Chem., Vol. 3, Aug., 1911. When the sulphate is 25 p.p.m. or more, the determination may be made by the turbidimeter method direct on 100 cc. For less quantities, larger amounts of water are taken and evaporated.

### Sodium and Potassium

The filtrate contains sodium and potassium and may be used for such unless the water is highly mineralized, in which case a new portion, 100 cc. to 500 cc., should be taken.

Evaporate to dryness, add saturated solution of barium hydrate in excess, filter, wash with hot water, add to the filtrate ammonium carbonate in excess and a few drops of ammonium oxalate, boil, filter, evaporate again to dryness and dry at a high temperature to expel excess of ammonia salts. Redissolve, add slight excess of ammonium carbonate again and continue until no further precipitate is formed on such addition. Evaporate to dryness in a weighed platinum dish, remove ammonium salts by high-temperature drying, and weigh the combined chlorides of sodium and potassium. Moisten with about 25 cc. of water and a few drops of HCl and add from 1 cc. to 5 cc. of 10% solution of platinic chloride

<sup>1</sup> Freidbaum and Nydegger, Z. Agnew. Chem., 1907-9.

(1 cc. to each 25 milligrams to 30 milligrams total chlorides). Evaporate to dryness on water bath, take up and wash with 95% alcohol until filtrate is free from color. Dry, redissolve precipitate, washing through the filter paper in hot water. Evaporate again to dryness and weigh as  $K_2PtCl_6$ .

$$K_2PtCl_6 \times .161 = K.$$

$$K_2PtCl_6 \times .307 = KCl.$$

Deduct from combined weight of chlorides. Remaining  $NaCl \times .394 = Na$ .

NOTE. When separation is not necessary, the combined chlorides are calculated as sodium chloride and reported as sodium and potassium chlorides.

### Alkalinity

In ordinary cases titrate with N/10 or N/50  $H_2SO_4$ , using methyl orange as indicator. Special cases will be considered later.

Reagents. Sulphuric acid, N/10. Methyl orange. Phenolphthalein.

Operation. 250 cc. of water in 400-cc. beaker or a casserole are titrated with N/10  $H_2SO_4$ , using two to five drops of methyl orange indicator (or 50 cc. can be similarly titrated with N/50  $H_2SO_4$ ).

Calculate for 250-cc. sample.

$$\text{No. cc.} \times 4 \times .005 = \text{gms. per liter } CaCO_3.$$

$$\text{No. cc.} \times 4 \times 58.4 \times .005 = \text{grs. per gallon } CaCO_3.$$

$$\text{Or } \times 1.168 = \text{grs. per gallon } CaCO_3.$$

Distilled water, and neutral waters containing magnesium chloride and magnesium sulphate frequently give an alkaline reaction when used with methyl orange. In such cases from .2 to .8 cc. N/10 acid are required to discharge the alkaline color of the methyl orange. Such a procedure would suggest to the operator that the waters were alkaline. However, if such neutral waters are boiled with phenolphthalein as an indicator for twenty minutes and no pink color develops, the waters are not alkaline but neutral. The use of a blank of .2 cc. is of no value under such conditions and it appears to the writer as much the safest way when the titration is under 1 cc. of N/10 acid that the water be boiled with phenolphthalein in an effort to determine absolutely whether this water is alkaline, due to the presence of a carbonate as indicated by the methyl orange, or whether the alkalinity is entirely due to the hydrolyzing of the calcium or magnesium base present in the absence of alkali. When no pink color is produced the water should be pronounced neutral.

Phenolphthalein may also be used as indicator on another 250-cc. portion, using the above procedure. This titration in connection with the methyl orange titration makes possible a determination of the relation of carbonate, bicarbonate and caustic alkalinity.

The following is adapted from a table on page 39, Standard Methods of Water Analysis of the American Public Health Association, and is of value in showing the relation of the various titrations. Methyl orange has been used in place of erythrosine.

TABLE SHOWING RELATION BETWEEN ALKALINITY BY PHENOL-PHTHALEIN AND THAT BY METHYL ORANGE IN PRESENCE OF BICARBONATES, CARBONATES AND HYDRATES.

	Bicarbonates.	Carbonates.	Hydrates.
$P = O$ . . . . .	M	O	O
$P < \frac{1}{2}M$ . . . . .	$M - 2P$	$2P$	O
$P = \frac{1}{2}M$ . . . . .	O	$2P$	O
$P > \frac{1}{2}M$ . . . . .	O	$2(M - P)$	$2P - M$
$P = M$ . . . . .	O	O	M

M = Methyl orange alkalinity.  
P = Phenolphthalein alkalinity.

### Acidity

For acidity use N/10  $\text{Na}_2\text{CO}_3$  and 250 cc. water.

Acidity due to	Indicator.	Hot or Cold.
Carbonic and sulphuric acids, also Fe and Al sulphates. . . . .	Phenolphthalein	Cold
Sulphuric acid, also Fe and Al sulphates. . . . .	Phenolphthalein	Boiling
Sulphuric acid alone . . . . . When desired, 20 cc. N/10 $\text{H}_2\text{SO}_4$ may be added. Boil fifteen to twenty minutes, cool and titrate, noting the excess of acidity over the original 20 cc.	Methyl orange	Cold

### Free Carbonic Acid <sup>1</sup>

**Reagents.** Either standard N/10 sodium carbonate or standard N/22 sodium carbonate. For the latter dissolve 2.41 grams of dry sodium carbonate in one liter of distilled water which has been boiled and cooled in a carbon dioxide free atmosphere. Hold both solutions in glass bottles protected by tubes filled with soda-lime.

One cc. N/10  $\text{Na}_2\text{CO}_3 = 2.2$  milligrams  $\text{CO}_2$ .

One cc. N/22  $\text{Na}_2\text{CO}_3 = 1.0$  milligram  $\text{CO}_2$ .

**Operation.** With N/10 sodium carbonate titrate 250 cc. of sample in 400-cc. beaker, using phenolphthalein as indicator. First faint but permanent pink denotes end-point.

Using 250 cc.

No. cc. N/10  $\text{Na}_2\text{CO}_3 \times 8.8 = \text{CO}_2$  parts per million.

No. cc. N/10  $\text{Na}_2\text{CO}_3 \times .513 = \text{CO}_2$  grains per gallon.

With N/22 sodium carbonate solution, use 100 cc. of sample, preferably in 100-cc. Nessler tube, titrate and rotate the tube until faint but permanent

<sup>1</sup>For criticisms of this method see Z. Nahr. Genussm., 24, 429, also Chem. Abs., 4, 1024; C.A., 6, 3137; C.A., 7, 38.

pink color 30 seconds without fading is produced, using phenolphthalein as indicator

Using 100 cc.

No. cc.  $N/22 \text{ Na}_2\text{CO}_3 \times 10 = \text{CO}_2$  parts per million.

No. cc.  $N/22 \text{ Na}_2\text{CO}_3 \times .583 = \text{CO}_2$  grains per gallon.

### Chlorine

Titrate 100 cc. of water, using 1 cc. of 10% potassium chromate as an indicator, with  $N/10 \text{ AgNO}_3$  to first permanent indication of the red silver chromate. (Acid waters should be neutralized and sulphide waters boiled with a drop or so of nitric acid and then neutralized for reliable results.)

No. cc.  $\times 3.42 = \text{grs. per gallon NaCl}$ .

No. cc.  $\times 58.46 = \text{parts per million NaCl}$ .

No. cc.  $\times 35.46 = \text{parts per million Cl}$ .

**NOTE.** Where qualitative test shows chlorine to be high, smaller portions of the sample should be taken, either by certified pipette, or burette, and when the titration with  $N/10 \text{ AgNO}_3$  is less than .2 cc.,  $N/50$  or  $N/100 \text{ AgNO}_3$  should be used for accuracy.

### Nitrates

(Also see Sanitary Analysis)

Evaporate 100 cc. of water, after adding 2 cc. 10%  $\text{Na}_2\text{CO}_3$ , to dryness, cool, moisten with 2 cc. phenolsulphonic acid, add 50 cc. water and then  $\text{NH}_4\text{OH}$  until slightly ammoniacal. Yellow coloration shows presence of nitrates. Compare with standards which should be renewed every month, or oftener. Less than  $\frac{1}{8}$  grain per gallon, or about 2 parts per million as  $\text{KNO}_3$ , while of value in sanitary analyses, usually rank as "trace" in mineral waters.

Where nitrates are high, 85 to 90 parts per million, or 5 grains per gallon and over, colorimetric methods do not always give reliable results, and 500 cc. of the water should be first boiled with a slight excess of acid, then made alkaline with sodium or potassium hydroxide, reduced with 10 grams each of powdered Zn and Fe, or 10 grams powdered Al, and distilled into an excess of  $N/10$  or  $N/100 \text{ HCl}$ , as the case may be, and titrated back, using cochineal as indicator, and calculating the ammonia absorbed to  $\text{NO}_2$  or  $\text{Ca}(\text{NO}_3)_2$  as desired. (Where free ammonia or its compounds are present corrections must be made.)

A recent modification of this method depends upon the absorption of ammonia into a solution of boric acid (5 grams boric acid in 100 cc. of water). Due to the very weak acidity of the boric acid, it is possible to titrate the ammonia direct with standard acid, using methyl orange as an indicator, and this has the advantage of doing away with two standard solutions. The boric acid strength is based upon 5 grams of boric acid to 100 cc. of water to each .2 gram of ammonia absorbed. It is stated that even the cooled condenser is unnecessary, in this absorption.<sup>1</sup>

<sup>1</sup> The Volumetric Determination of Ammonia. L. W. Winkler, Budapest. *Z. angew. Chem.*, 26, Aufsatzteil, 231-2.

Determination of Ammonia by the Boric Acid Method. L. W. Winkler, *Z. angew. Chem.*, 27, I, 630-2, 1914.

The Determination of Ammonia by the Boric Acid Method. E. Bernard, *Z. angew. Chem.*, 27, I, 664, 1914.

### Ammonia and Its Compounds

Place 500 cc. or less in an 800-cc. Kjeldahl flask, make alkaline and distill into N/10, or weaker, HCl, titrate with cochineal or Nesslerize. (See Sanitary Analysis, page 536.)

### Total Mineral Residue

Use a clean weighed platinum dish. Evaporate 50 cc. (certified pipette) to dryness at about 130° C. and bake for at least thirty minutes at that temperature. Ordinary water-bath temperature will not remove water of crystallization from  $\text{Na}_2\text{SO}_4$  or  $\text{CaSO}_4$ . Weigh to the fourth decimal or .0001 gram.

$\text{Weight} \times 1168 = \text{grains per gallon.}$

$0.1 \text{ milligram} = 2 \text{ parts per million.}$

Residues of acid waters should be ignited to a dull red heat. Where the acidity is low a drop or so of sulphuric acid should be added to assure the fixation of all sodium and potassium salts as the sulphate. The ignition should be complete so that no free acid is left behind and to assure the decomposition of all iron compounds to the oxide form. In calculating, correction must be made for the change in the iron salts and all other compounds converted to the sulphate form for comparison with the sulphated residue, and then the proper corrections made to give the theoretical residue on the original water.

Residues with much organic matter, after weighing, may be gently ignited until the carbon has been burned off, cooled, recarbonated with tested  $(\text{NH}_4)_2\text{CO}_3$ , dried and again weighed. The difference in weight after titrating for possible volatilized chlorides gives approximately the organic matter present.

Waters high in easily decomposed  $\text{MgCl}_2$  or  $\text{Ca}(\text{NO}_3)_2$  should be evaporated with a few drops excess of  $\text{H}_2\text{SO}_4$  or  $\text{Na}_2\text{CO}_3$ , and the residue compared with an addition of all bases calculated to the sulphate form, or corrected for added carbonate.

**NOTE.** When acid is used, ignite to a dull red heat; when carbonate, evaporate as in the case of the original residue.

### Hydrogen Sulphide

Due to the fact that hydrogen sulphide is frequently very transient and often oxidizes to sulphate in transit, it is advisable to collect this sample in a special container at the point of sampling. Two or three bottles holding exactly 250 cc. of water each, are used, each bottle containing 50 cc. N/100 iodine solution. After filling, the bottle is sealed. The sample is titrated with standard N/100 sodium thiosulphate upon receipt at laboratory, at which time a blank is run, using 50 cc. iodine solution made to mark with distilled water. The difference between the titration of the sample and the blank represents hydrogen sulphide present.

$\text{Iodine value} \times 0.1263 \times 4 = \text{sulphur value grams per liter.}$



## Oil

Frequently waters from condensing engine, or after passing heaters or oil separators, still contain oil in small quantities. The following method has been found most satisfactory:

**Reagents.** *Ferric Chloride Solution.* (10 grams of iron dissolved in 200 cc. HCl, oxidized with HNO<sub>3</sub> and made to one liter.)

*Ammonia* C.P.

**NOTE.** If the oil exceeds 0.4 grain per gallon, use 500 cc., or less for the determination; if below 0.4 grain per gallon use 1 liter.

**Operation.** Add to the water taken in a large beaker or flask 5 cc. of the "ferric chloride" solution and heat nearly to boiling; then add ammonia in excess, to precipitate the iron (which precipitate contains all the oil), and boil for two minutes.

Allow to stand a few minutes and filter through a 15 cm. filter paper which has been previously extracted with ether, transferring the precipitate on to the paper with hot water, and washing three or four times with hot water. Then dry both filter and precipitate in the water oven at 100° C. and when dry, extract with ether in the soxhlet in the usual way, evaporate the ether extract and weigh the remaining oil.

## Dissolved Oxygen

Use the Winkler Method<sup>1</sup>

**Reagents.** No. 1. *Manganous Sulphate Solution.* 48 grams manganous sulphate dissolved in 100 cc. distilled water.

No. 2. *Iodide Solution.* 360 grams NaOH and 100 grams KI dissolved in 1 liter of distilled water.

No. 3. *Concentrated hydrochloric acid, or sulphuric acid sp.gr. 1.4 (dilute 1 : 1).*

No. 4. *Sodium Thiosulphate Solution.* N/100 solution is made as needed from the N/10 stock solution.

**NOTE.** Not permanent; should be frequently restandardized against N/100 potassium bichromate.

The addition of 5 cc. of chloroform plus 1.5 grams sodium or ammonium carbonate to each liter of solution on mixing will improve its keeping quality.

N/40 sodium thiosulphate containing 6.2 grams C.P. recrystallized salt per liter may be preferred to N/100 strength. 1 cc. of this solution is equivalent to 0.2 milligram oxygen by weight or 0.1395 cc. oxygen by volume, standard conditions.

5. *Starch Solution.*<sup>2</sup> The starch should first be made into a thin paste with cold water and about 200 times its weight of boiling water stirred in and boiled for a few minutes. A few drops of chloroform will assist in preserving this solution.

**Collection of Sample.** A small-necked, 250-cc. bottle should be used, etched or otherwise marked, with its exact volume previously determined. The collec-

<sup>1</sup>Ber. deutsche Chem. Gesell., 21, 2843, 1888. Also Z. Anal. Chem., 53, 665-72, 1914; C.F.C.A., 8, 674, 1915.

<sup>2</sup>Hale gives the following method. "Rub 5 grams of potato starch with cold water to a thin paste together with 10 milligrams of mercuric iodide. Pour into one liter of boiling water and boil half an hour."

tion should be so arranged to exclude outside air and result in several continuous changes of the contents before stoppering, care being taken to exclude air bubbles.

**Operation.** To sample as received add, in both cases by pipette, delivering below surface of water and away from the air, 2 cc. solution No. 1 (manganese sulphate) and No. 2 (NaOH, KI). Restopper and shake thoroughly. After precipitate has settled add 2 cc. HCl or  $H_2SO_4$  and again mix by thorough shaking until precipitate has completely dissolved, transfer 100 cc. to flask, and titrate with solution No. 4 (sodium thiosulphate), using starch as indicator near end as the color approaches a faint yellow.

N = cc. N/100 thiosulphate solution.

V = capacity of bottle less 4 cc. (vol. sol. 1 and 2 added).

O = the amount of oxygen in parts per million in water saturated at the same temperature and pressure.

$$(1) \text{ Oxygen in p.p.m.} = \frac{.0008N \times 1,000,000}{100} = .8N.^1$$

$$(2) \text{ Oxygen in cc. per liter} = .7 \text{ oxygen p.p.m.}$$

$$(3) \text{ Oxygen per cent saturation} = \frac{\text{Oxygen p.p.m. (observed temp. and pres.)}}{\text{Saturation oxygen p.p.m. (observed temp. and pres.)}}$$

## METHODS FOR THE DETERMINATION OF SMALL AMOUNTS OF LEAD, ZINC, COPPER AND TIN

Very frequently a determination is desired of materials which are apt to be present in water due to the solvent action of such water upon pipes and containers. In most cases the estimates are made by colorimetric methods if the amounts present are exceedingly small. As these determinations are made only in rare cases it seems advisable to summarize, calling attention to the fact that all methods may be found in full in any of the editions of Standard Methods for Water Analysis gotten out by the American Public Health Association.

Where any or all of the metals, lead, zinc, copper and iron are apt to be present, a large quantity (1 to 4 liters), of the water is evaporated. The metals are separated as sulphides with ammonia and hydrogen sulphide. The precipitate after washing is dissolved in nitric acid and refiltered to remove suspended matter and then concentrated with  $H_2SO_4$ .

The lead is removed by taking up the concentrated solution with 50% alcohol (100 cc. to 150 cc.), filtering and dissolving the precipitate in ammonium acetate, after which the solution is made to volume and divided. One-half is saturated with hydrogen sulphide water to get an approximate idea of the amount of lead present. To the other half add two to three drops of acetic acid, then an excess of hydrogen sulphide water and compare the color with standards. This gives lead.

The alcohol is removed from the filtrate by evaporation and it is then treated with ammonia to remove possible iron. The filtrate from the iron precipitate

<sup>1</sup>Correcting for displacement for 300-cc. bottle,  $.8N = .811N$ ; for 275-cc. bottle,  $.8N = .812N$ .

No correction for displacement affects result .1 p.p.m. oxygen.

Twenty-five cc. variation in capacity of bottle affects result .01 p.p.m. oxygen.

The above formulæ are based upon N/100 thiosulphate, and titrating 100 cc. volume. N = cubic centimeters thiosulphate used.

is neutralized with  $H_2SO_4$ , then 2 cc. concentrated  $H_2SO_4$  and 1 gram urea added. Copper is removed by electrolyzing (two hours with 0.5 ampere current). If the deposit is material it may be weighed as copper after washing with alcohol and drying. When the deposit is extremely small it should be dissolved in nitric acid, evaporated to dryness to remove acid taken up in water, after which potassium sulphide solution is added and the color compared with standards. This gives *copper*.

The solution from the above is nearly neutralized with ammonia. It is then concentrated and 2 grams potassium oxalate and 1.5 grams potassium sulphate are added and the zinc removed by electrolyzing. (Three hours with 0.3 ampere current.) This gives *zinc*.

Where copper only is desired it is frequently sufficiently satisfactory to concentrate the water from 50 cc. to 75 cc., after which it is acidified with 2 to 5 cc. concentrated  $H_2SO_4$ , depending upon whether the water is very alkaline with carbonate of lime, etc., and then the procedure for copper is followed.<sup>1</sup>

There is no satisfactory method for the quantitative determination of small quantities of tin. In the above-mentioned procedure, however, in case tin should be present it would be removed with the ammonia precipitate for the removal of iron and its presence may be avoided by dissolving the sulphides in the original precipitation in  $HNO_3$ , in which the tin would remain behind insoluble.

## HARDNESS

### Total Hardness

The most accurate method for total hardness is by calculation of the calcium and magnesium determined gravimetrically as previously outlined, calculating the calcium as calcium carbonate and the magnesium to its calcium carbonate equivalent in terms of parts per million.<sup>2</sup> However, where only the hardness is desired, gravimetric methods are cumbersome and the following are accepted as standard.

The standard method for the determination of total hardness, as well as temporary and permanent, depends upon the action of the lime and magnesia in solution upon soap, the soap added in a very dilute solution in alcohol. Total hardness represents the total soap acted upon by the water in its original state, permanent hardness represents the total soap acted upon by the water after the water in question has been thoroughly boiled and separated from the suspended matter, and temporary hardness represents the difference between the total hardness and the permanent hardness, and while it is supposed to represent combined carbonates of lime and magnesia, and the permanent hardness is supposed to represent lime and magnesia in other forms than carbonate, this is rarely so due to the fact that a certain material amount of carbonate of lime and magnesia is soluble in water, even in the absence of carbon dioxide gas. The reagents used are *standard soap solution* and *standard calcium chloride solution*, the latter being made under such conditions that 1 cc. of the solution is equivalent to 0.2 milligram of calcium carbonate.

<sup>1</sup> Phelps, Jour. Amer. Chem. Soc., 28, 369, 1906.

<sup>2</sup> C. Bahlmann, J. Ind. Eng. Chem., 6, 209, 11.

### Preparation of Solutions

0.2 gram pure calcium carbonate is dissolved in a small amount of dilute HCl, taking pains to avoid any loss due to effervescence or spattering. Evaporate the solution to dryness several times to remove excess acid. Dissolve in distilled water and make up to 1 liter.

*Standard soap solution* is obtained by dissolving approximately 100 grams dry castile soap in 1 liter 80% alcohol. This solution should stand several days. For standardizing, this solution should be diluted with alcohol (70% to 80%), until 6.4 cc. when added to 20 cc. of standard calcium solution will produce a permanent lather. Usually less than 100 cc. of the original soap solution will make 1 liter of standard solution.

For standardizing, use 250-cc. glass-stoppered bottle, add 20 cc. calcium solution with 30 cc. distilled water. The soap solution should be added from a burette, approximately .2 cc. at a time, after which the bottle is shaken vigorously until the lather formed remains unbroken for five minutes after shaking and after the bottle has been placed upon its side.

**NOTE.** Pure potassium oleate and potassium carbonate may be used in place of soap.<sup>1</sup>

**Operation.** Fifty cc. of the water in question are measured into a 250-cc. bottle, the soap solution added, approximately .2 cc. at a time, and in the same manner as described for the standardizing of said soap solution. The following table, copied from p. 33, *Standard Methods of Water Analysis*, A.P.H.A., 1913, may be used to obtain the total hardness from the results so noted:

TABLE OF HARDNESS SHOWING THE PARTS PER MILLION OF CALCIUM CARBONATE ( $\text{CaCO}_3$ ) FOR EACH TENTH OF A CUBIC CENTIMETER OF SOAP SOLUTION WHEN 50 CC. OF THE SAMPLE ARE USED.

cc. of Soap Solution.	0 0 cc.	0 1 cc.	0 2 cc.	0 3 cc.	0 4 cc.	0 5 cc.	0 6 cc.	0 7 cc.	0 8 cc.	0 9 cc.
0.0	....	....	....	....	....	....	....	0 0	0 6	3.2
1.0	4 8	6.3	7.9	9.5	11.1	12.7	14.3	15 6	16.9	18.2
2.0	19 5	20 8	22 1	23.4	24 7	26.0	27 3	28 6	29.9	31.2
3.0	32 5	33 8	35 1	36 4	37 7	38 0	40 3	41.6	42.9	44.3
4.0	45 7	47.1	48 6	50 0	51 4	52 9	54 3	55 7	57.1	58.6
5.0	60 0	61 4	62 9	64 3	65 7	67.1	68 6	70.0	71.4	72 9
6 0	74.3	75.7	77 1	78 6	80 0	81 4	82 9	84.3	85 7	87 1
7.0	88.6	90 0	91.4	92 9	94.3	95 7	97.1	98.6	100 0	101.5

It is not desirable to use more than 7 cc. of soap solution for 50 cc. of the water, and when the figures are higher, the water should be diluted with distilled water. The reading in the table corresponding to the cc. of soap solution

<sup>1</sup>C. Blacher, *Chem. Ztg.*, **36**, 541; *J. Soc. Chem. Ind.*, **31**, 555, *C. A.*, **7**, 1394; C. Blacher, P. Gruenberg, M. Kissa, *Chem. Ztg.*, **37**, 56-8, *C. A.*, **7**, 1938. L. W. Winkler, *Z. Anal. Chem.*, **53**, 409-15, *C. A.*, **8**, 2912.

used is then multiplied by the quotient  $\frac{50 \text{ cc.}}{x \text{ cc.}}$ ;  $x$  cc. being equal to the amount of water taken. In making this determination there is frequently noted a false end-point sometimes known as the magnesium end-point. To avoid error, it is advisable, after completing the titration, to read the burette, add 0.5 cc. more of the soap solution and shake well. If magnesium has been responsible for the false end-point, after such addition the lather will again disappear, and titration should be continued until a new and true end-point is reached. It is advisable to determine the strength of the soap solution from time to time, as it is very prone to change upon standing. Results should be recorded in terms of calcium carbonate, parts per million. There are various other means of reporting. The English degree frequently noted as Clark degree, represents grains calcium carbonate per Imperial gallon and should be multiplied by 14.3 to give parts per million. Conversely, the result obtained in parts per million divided by 14.3 will give Clark, or English degrees. French degrees represent parts per 100,000 calcium carbonate and should be multiplied by 10 to give parts per million. Conversely, division of the result obtained above by 10 will give French degrees. German degrees represent parts per 100,000 calcium oxide and should be multiplied by 17.8 to give parts per million calcium carbonate. The determination of hardness is not reliable on account of the varying action of calcium and magnesium salts, and should never be resorted to when possible to determine these bases direct.

NOTE. Dr. Hale claims that the soap method for hardness in skilled hands is accurate from 10 to 15 parts per million on waters as hard as 300 parts.

For *permanent hardness* the standard soap solution is used as above stated. The water, however, is boiled gently for one-half hour, allowed to cool, made to volume with boiled and cooled distilled water and filtered, after which the above method is used. The difference between total hardness and permanent hardness is supposed to represent temporary hardness. The *alkalinity* determination given on a previous page is a much more accurate method of determining temporary hardness, however, and is also much more easily carried out. When total hardness and alkalinity are determined, permanent hardness would be the difference between these two figures. For comparative use as against *total* and *permanent* hardness determined as such, the results would be much different, as the alkalinity determination of all the carbonates would give a permanent hardness representing absolutely non-carbonate hardness; whereas the determined permanent hardness would contain a material amount of combined carbonates of lime and magnesia. The American Public Health Association, Committee on Standard Method of Water Analysis, recommend that the determination of permanent hardness by the soap solution be discontinued in connection with softening process, as it is so unsatisfactory in general practice.

### Magnesium Chloride

Frequently, when hypothetical combinations are used it is desired to check up these calculated combinations by some chemical method. Magnesium chloride is frequently produced in the course of hypothetical combinations and its presence is as frequently a source of much trouble in the determination of a mineral residue, owing to the ease with which it decomposes or carbonates. A method is suggested

whereby a second 50 cc. portion similar to the total mineral residue is exactly neutralized with sufficient  $H_2SO_4$ , the amount to use being calculated from the total alkalinity obtained elsewhere. The solution is allowed to go to complete dryness, is baked at a temperature of  $280^{\circ} F.$  to  $300^{\circ} F.$ , and after being cooled the chlorine is titrated. The difference between the chlorine thus determined and the total chlorine previously determined represents chlorine lost by volatilization as magnesium chloride. In the absence of organic matter this method is approximately accurate. Where organic matter or other reducing material is present, however, the results are not so satisfactory.

### Calcium Sulphate

In a similar manner it is frequently desired to know whether or not a water would contain calcium sulphate, and a method of comparative satisfaction depends upon the evaporation of 250 cc. to 500 cc. of the original water to dryness. After cooling, 10 cc. of distilled water are added and the mineral matter loosened from the sides of the dish and partially dissolved. Ten cc. of 95% alcohol are then added and 100 cc. of 50% alcohol. After thorough stirring and solution this material is filtered, the precipitate washed with 50% alcohol and the filtrate made to volume, divided and tested for calcium and sulphates in the usual manner. The method is only approximate.

### LIME AND SODA VALUE<sup>1</sup>

Two very simple methods have been devised for the rapid estimation of the amount of lime and soda-ash necessary for softening, when water treatment is considered from the outside softening-plant point of view.

#### Value for Lime

**Reagents.** Saturated lime water (strength to be known for each series of determinations). *N/10 hydrochloric acid.*

**Process.** Take 200 cc. of the water in question; add 50 cc. saturated lime-water solution in 250-cc. volumetric flask and heat to boiling. Allow to cool. Fill to the 250-cc. mark with water to replace that lost by evaporation; filter through a dry-folded filter and titrate 200 cc. of the filtrate with *N/10* acid, using methyl orange as an indicator.

For calculation, let "a" equal number of cc. *N/10* calcium oxide in 50 cc. the lime water, as determined; and let "b" equal the number cc. *N/10* hydrochloric acid used in determination.

$(4a - 5b) \times 3.51$  CaO will give milligrams of lime per liter required to soften the water tested.

#### Value for Soda

To the neutralized 200 cc. from above titration, add 20 cc. *N/10* sodium carbonate. Heat to boiling. Transfer with  $CO_2$  free distilled water into a 250-cc. flask to make up to mark with washings from the dish; mix thoroughly and filter, collecting 200 cc. of the filtrate in a beaker. Titrate with *N/10* hydro-

<sup>1</sup> Drawe, *Zeit. f. Angew. Chem.*, **23**, 52, 1910.

chloric acid for the excess alkali. Designate the number of cc. in this titration by "c."

Formula:  $(20 - b - \frac{1}{2}c) \times 33.13 \text{ Na}_2\text{CO}_3$  = milligrams of soda per liter necessary to soften water in question.

NOTE. Both formulæ are based upon C. P. chemicals, and corrections must be made for the value of the commercial materials in use. These methods are valuable, though for actual practice it is advisable to try out on a liter of water in question, using the calculated amounts of lime and soda for experimental purposes.

## METHODS OF REPORTING AND INTERPRETATION

The manner of reporting the results of a mineral analysis of any water calls for as much thought and uniformity as the methods of analysis themselves, and in this department there is much less uniformity than in the case of analytical methods. Undoubtedly, the ideal method of reporting is that which gives results in Ionic form (positive and negative radicals), in terms of parts per million or grains per gallon. The latter term is purely American and would have to be converted for comparison with results obtained in almost any foreign country. Parts per million, though newer and still unfamiliar to all but professional and scientific men, is gaining gradually a strong foothold, and the consideration of this terminology with the Ionic form of reporting will be considered prior to the discussion of hypothetical combination and grains per gallon.

Mr. Herman Stabler,<sup>1</sup> and R. B. Dole,<sup>2</sup> of the United States Geological Survey, have devised and simplified certain calculations and formulas, which greatly assist in the interpretation, comparison, and classification of waters for Industrial and Irrigation<sup>3</sup> purposes. Formulas with reference to dissolved solids will be the only ones discussed here. The following table gives reaction coefficients:

Positive Radicals.	Reaction Coefficients.	Negative Radicals.	Reaction Coefficients.
Ferrous Iron (Fe).....	0.0358	Carbonate (CO <sub>3</sub> ).....	0.0333
Aluminum (Al).....	.1107	Bicarbonate (HCO <sub>3</sub> ).....	.0166
Calcium (Ca).....	.0499	Sulphate (SO <sub>4</sub> ).....	.0208
Magnesium (Mg).....	.0822	Chlorine (Cl).....	.0282
Sodium (Na).....	.0435	Nitrate (NO <sub>3</sub> ).....	.0161
Potassium (K).....	.0256		
Hydrogen (H).....	.992		

Using the above table, the parts per million of each radical multiplied by its reacting coefficient will give its reacting value, and in the formulas which follow this will be indicated by "r" prefixed to the chemical symbol of the radical.

For checking the accuracy of the analysis, the sum of the positive reacting values should equal the sum of the negative reacting values, and the formula,

$100 \frac{r. \text{ Pos.} - r. \text{ Neg.}}{r. \text{ Pos.} + r. \text{ Neg.}} = E$ , the percentage error of the analysis. The value of this error should never exceed 5 for waters of 100 p.p.m. or more dissolved solids, and should be 2 or less.

<sup>1</sup> Eng. News, 60, 355, 1909.

<sup>2</sup> Water Supply Paper No. 274, p. 165, Water Supply Paper No. 254, J. Ind. and Eng. Chem., 6, (1914), No. 7, p. 710.

<sup>3</sup> U. S. G. S. W. S. Paper, 274, p. 177.

In ordinary analysis, silica, iron and aluminum are present in such small quantities that they may, for simplicity's sake, be ignored. The following formulas are given without comment, as full details can be found in Water Supply Paper No. 274.

### Water Softening

**For 1000 Gals. Water.** Pounds lime (90% CaO) required  
 $= 0.26(r\text{Fe} + r\text{Al} + r\text{Mg} + r\text{H} + r\text{HCO}_3 + .0454 \text{CO}_2).$

Pounds soda ash (95%  $\text{Na}_2\text{CO}_3$ ) required  
 $= 0.465(r\text{Fe} + r\text{Al} + r\text{Ca} + r\text{Mg} + r\text{H} - r\text{CO}_2 - r\text{HCO}_3).$

**NOTE.** Dr. Hale states the following. Instead of the extended formulae of the ionic system, I much prefer my simple formulae.

$(\text{Alkalinity} \times .44 + \text{free CO}_2) \times .0108 = \text{lbs. CaO per 1000 gals. feed water.}$

**Also**  $(\text{Total hardness} - \text{total lime}) \times .0047 = \text{lbs. CaO per 1000 gals. feed water.}$   
 or total magnesia as  $\text{CaCO}_3$ .

$(\text{Total hardness} - \text{alkalinity}) \times .009 = \text{lbs. Na}_2\text{CO}_3 \text{ per 1000 gals. feed water.}$   
 Expressed as  $\text{CaCO}_3$ .

### Foaming and Priming

Foaming coefficient  $F = 2.7 \text{ Na.}$

Taking into consideration the various boilers and the action of various waters in practice, the following approximate classification of waters for foaming conditions is of value:

Non-foaming,  $F = 60$  or less.  
 Semi-foaming,  $F = 60-200$ .  
 Foaming,  $F = 200$  or more.

### Corrosion

#### *For Acid Waters*

Coefficient of corrosion  $C = 1.008(r\text{H} + r\text{Al} + r\text{Fe} + r\text{Mg} - r\text{CO}_2 - r\text{HCO}_3).$

#### *For Alkaline Waters*

$C = r\text{Mg} - r\text{HCO}_3.$

If  $C$  is positive, water will corrode.

If  $C + .0503 \text{ Ca}$  is negative, water will not corrode on account of the mineral materials in the water.

If  $C$  is negative, but  $C - .0503 \text{ Ca}$  is positive, the water may or may not corrode.

### Scale

$\text{SiO}_2 + 2.95 \text{ Ca} + 1.66 \text{ Mg} = \text{scale p.p.m.,}$

or

$^1 (.00833 \text{ Sm} + .00833 \text{ Cm} + .3 r\text{Fe} + .142 r\text{Al}) + .168 r\text{Mg} + .492 r\text{Ca}$   
 $= \text{scale lbs. per 1000 gallons.}$

<sup>1</sup> Can be omitted or ignored unless suspended matter, silica, etc., are present in large quantities.



There are also formulas given in the above-mentioned Bulletin on soap cost, lime, soda, soda ash, cost hard scale (pounds per 1000 gallons) and a hardness coefficient of the scale formation.

### Irrigating Waters

#### *Alkali Coefficient*

(a) When  $\text{Na} - .65 \text{ Cl}$  is zero or negative.

$$\text{Alkali coefficient, } k = \frac{2040}{\text{Cl}}.$$

(b) When  $\text{Na} - .65 \text{ Cl}$  is positive, but not greater than  $.48 \text{ SO}_4$ .

$$\text{Alkali coefficient, } k = \frac{6620}{\text{Na} + 2.6 \text{ Cl}}.$$

(c) When  $\text{Na} - .65 \text{ Cl} - .48 \text{ SO}_4$  is positive,

$$\text{Alkali coefficient, } k = \frac{662}{\text{Na} - .32 \text{ Cl} - .43 \text{ SO}_4}.$$

Classification on basis of alkali coefficient:

Alkali coefficient.	Class.	Remarks.
More than 18 .	Good...	Have been used successfully for many years without special care to prevent alkali accumulation.
18 to 6.....	Fair. .	Special care to prevent gradual alkali accumulation has generally been found necessary except on loose soils with free drainage.
5.9 to 1.2.....	Poor...	Care in selection of soils has been found to be imperative and artificial drainage has frequently been found necessary.
Less than 1.2...	Bad. .	Practically valueless for irrigation.

### Hypothetical Combinations

The use of hypothetical combinations in the reporting of a mineral water is frequently of value, in that it gives a more rapid way of placing in simpler terms the principal materials present in the water. It should never be assumed from the hypothetical combinations that the materials so reported are present in the water in that particular form, but it is assumed by most, that the form in which such materials are reported will represent the condition in which those materials will combine when the water is subjected to increased pressure and increased temperature. In other words, the hypothetical combinations most generally in use represent the way materials will appear when combined, due to the law of mass action under steam-boiler conditions.

For such purpose the method which takes care of the insoluble materials or materials leaving the water first is the most common method in use. This method combines as follows: Where the sum of the sulphate and carbonate radicals exceeds that of lime and magnesia as bases, the magnesia is first calculated to carbonate, the remaining carbonate is combined with lime, the remaining lime

with sulphate and the remaining sulphate with sodium. This also takes care of the general condition where the carbonates alone are in excess of the combined carbonates of lime and magnesium, in which case the remaining carbonate naturally would be calculated to sodium and all the sulphate, as well as chloride, also, calculated to sodium. Where, however, the sum of the bases is greater than the sum of the carbonate and the sulphate radicals, two possible conditions or combinations exist. Where magnesium chloride is present in the water, the sum of the acids calculated to the soda radical should be greater than the total mineral residue. Partially decomposed magnesium chloride is indicated in this way, also the fact that magnesium chloride has a lower molecular weight than sodium chloride, which condition would be indicated in such a comparison. When this case exists, the sulphate is first calculated to calcium, the remaining calcium to carbonate, the remaining carbonate to magnesium, the remaining magnesium to chloride, the remaining chloride to sodium. Where the total mineral residue is greater than the sum of the acids and where nitrates are present, we then have nitrate of lime, which is assumed the commoner form than nitrate of magnesium, and the calculations are as follows: All the sulphate is calculated to lime, all the magnesium to carbonate, the remaining carbonate to lime, the remaining lime to nitrate, the remaining nitrate to sodium, and all the chlorides to sodium. In acid waters naturally the lime and magnesia, as well as the iron and aluminum, are calculated to the acid present in the greatest excess. These methods of calculation will give certain materials frequently found in scale formation and materials frequently supposed to cause certain characteristic troubles in either steam or domestic usage. It is possible in a purely qualitative way to judge or interpret the water on the basis of the lime and magnesium salts, for incrustation, and of the alkali salts for other troubles in boiler practice, also from the standpoint of irrigation, the various forms of the alkali salts as black and white alkali, without the necessity to use the formulas already considered.

### Field Assay of Water

Mr. R. B. Dole has published in Water Supply Paper No. 151, of the U. S. Geological Survey, field methods for the assay of water in which tablets of known value are used for the determination of chlorides, carbonates, sulphates and iron. In this type of assay, a given amount of the water is taken and tablets are added to the water until certain definite reactions take place, when the number of tablets used is estimated and an approximate value obtained. The error in such work varies from 3 to 15 per cent, but the results of the test give valuable, if not accurate, information.

The author is indebted to Dr. F. E. Hale, Director of Laboratories Department of Water Supply, New York City, for a careful review of this chapter, and for valuable suggestions.

# SANITARY ANALYSIS OF WATER

F. E. HALE.<sup>1</sup>

## THE MICROSCOPICAL EXAMINATION OF WATER SUPPLY

### Importance of the Determination

From the standpoint of palatability and of the aesthetic character of water supply there is no more important examination than the microscopical analysis. This examination discloses and measures the minute animal and plant life that is present in all surface waters and in some well waters.

Large amounts cause an unsightly turbidity and even relatively small quantities frequently cause complaint because of a scum produced when bath tubs are filled with hot water or of a stain left upon the sides of the white porcelain. The water of swimming pools, if unfiltered, may be unsightly. Industrial enterprises may be affected, for example the staining of clothes in laundries and interference with the manufacture of correct colors by dye manufacturers and with the dyeing of goods by the dyers. Photography may also be influenced.

The presence of certain types of microscopic organisms frequently serves to identify the source of a water, or indicate from what particular reservoir a supply may be drawn. In the case of New York City which serves to certain districts of Manhattan Borough water from the Croton supply, to other sections water from the Catskill supply and mixtures to others, the supply in any one section may be identified by the organisms as Catskill, Croton or a mixture. Again samples from cellars, excavations and conduits are frequently analyzed to determine whether the source is city water, sewage, or ground water. If microscopic organisms are present city water or sewage must be responsible and the chemical analysis and odor usually eliminate or indicate sewage. The contamination of a well supply by surface waters may be indicated by the presence of microscopic organisms.

The amounts of microscopic organisms bear a direct relationship to the various forms of nitrogen determined in the chemical analysis and frequently explain changes in these determinations.<sup>2</sup> As these growths increase free ammonia and nitrate decrease and albuminoid ammonia increases and as the growths decrease the reverse relationship holds.

The operation of filter plants, particularly the mechanical type, is much interfered with by heavy growths of microscopic organisms, the network of the latter interfering with the gelatinous formation of aluminum hydrate mechanical filters and the bacterial jelly of slow sand filters, although certain types of the diatoms may assist in the latter case.

<sup>1</sup> Director of Laboratories, Water Supply, Gas and Electricity, New York City.

<sup>2</sup> "The Significance of Nitrogen in its Various Forms in Water Supply." F. E. Hale, Proc. Am. W. W. Assoc., 1908, page 323-327.

By far the most important reason for determining microscopic organisms is their connection with disagreeable, sometimes vile, tastes and odors in water supply. Those so-called littoral growths, which are attached to the banks or bottoms of reservoirs, and which attract the quickest attention are not concerned as a rule. The trouble is caused by minute floating forms, which manufacture essential oils or perfumes like those of flowers. Exceedingly minute amounts produce pleasant aromatic geranium or grassy odors which become fishy, oily, pungent or vile in larger amounts or upon decay of the plant growths. Particular species may frequently be identified by the odor by those who are trained.

Three groups of odors are distinguished:

Aromatic (geranium) caused by Diatomaceae.

Grassy caused by Cyanophyceae.

Fishy caused by Chlorophyceae and a few Protozoa.

The following table as given by Whipple in "The Microscopy of Drinking Water" contains those organisms which have been at one time or another in sufficient quantity in a water supply to produce characteristic odors.

Group	Organism	Natural Odor
Aromatic Odor . . . . .	Diatomaceae:	
	<i>Asterionella</i> . . . . .	Aromatic-geranium-fishy.
	<i>Cyclotella</i> . . . . .	Faintly aromatic.
	<i>Dialoma</i> . . . . .	Faintly aromatic.
	<i>Meridion</i> . . . . .	Aromatic.
	<i>Tabellaria</i> . . . . .	Aromatic.
	Protozoa:	
	<i>Cryptomonas</i> . . . . .	Candied violets.
	<i>Mallomonas</i> . . . . .	Aromatic-violets-fishy.
	Cyanophyceae:	
Grassy Odor . . . . .	<i>Anabaena</i> . . . . .	Grassy and moldy, green-corn, nasturtiums, etc.
	<i>Ricularia</i> . . . . .	Grassy and moldy.
	<i>Clathrocystis</i> . . . . .	Sweet, grassy.
	<i>Coelosphaerium</i> . . . . .	Sweet, grassy.
	<i>Aphanizomenon</i> . . . . .	Grassy.
	Chlorophyceae:	
Fishy Odor . . . . .	<i>Volvox</i> . . . . .	Fishy.
	<i>Eudorina</i> . . . . .	Faintly fishy.
	<i>Pandorina</i> . . . . .	Faintly fishy.
	<i>Dictyosphaerium</i> . . . . .	Faintly fishy.
	Protozoa:	
	<i>Uroglena</i> . . . . .	Fishy and oily.
	<i>Synura</i> . . . . .	Ripe Cucumber, bitter and spicy taste.
	<i>Dinobryon</i> . . . . .	Fishy, like rockweed.
	<i>Bursaria</i> . . . . .	Irish moss-salt marsh-fishy.
	<i>Peridinium</i> . . . . .	Fishy, like clam-shells.
	<i>Glenodinium</i> . . . . .	Fishy.

In New York City's supply, despite the diversity of its sources, the only organisms which have given offense from odors have been *Asterionella*, *Tabellaria*, *Anabaena*, *Aphanizomenon* (with admixtures of *Clathrocystis*, *Microcystis*, and *Coelosphaerium*), *Uroglena*, *Synura*, and *Dinobryon*.

*Asterionella*, when present in 500 to 1000 standard units per cubic centimeter produces a slightly aromatic odor. At 1000 units, rarely less, the odor is distinctly similar to the odor of the geranium. The odor increases in intensity with increase in numbers until several thousand produce a fishy odor. The fishy odor is also produced when smaller quantities die.

*Tabellaria*, and similarly *Asterionella*, in very small amounts produces an earthy odor (also produced by large amounts of *Synedra*), passing through the aromatic, geranium and fishy stages with about the same relative quantities of organisms as *Asterionella*. At times the odor of *Tabellaria* has suggested illuminating gas, no other organisms being present. In the spring of 1919 extensive complaints of fishy taste in the Catskill supply were occasioned in New York City by only 700 units of *Tabellaria*. This was the result of intensification of odor by chlorination with liquid chlorine at Kensico reservoir. The odor was not noticeable in the water above the chlorination plant but appeared first just below the plant.

*Anabaena* and *Aphanizomenon*, when present in 500 to 1000 units, produce a faintly grassy odor like freshly-cut grass. With larger numbers the odor becomes pungent like nasturtium, or even onions. In large numbers, or when decaying, the odor is of vile, pigpen character. In the spring of 1918 from 500 to 800 units of *Aphanizomenon* in the Croton supply of New York City caused numerous complaints of an oily brown scum when bath tubs were filled with hot water. These complaints came chiefly from high class apartment houses.

*Uroglena* produces an oily fishy taste and odor, first noticeable in probably 500 to 1000 units. In larger quantities it is very disagreeable. The flavor is that of cod-liver oil.

*Synura* has caused trouble in as small amount as 300 units. The odor is variously described as like cucumber, muskmelon, etc. It leaves a bitter after-taste.

Troublesome organisms occur chiefly in surface waters. Occasionally well waters containing iron or manganese cause trouble from growths of *Crenothrix* and associated forms which clog pipes and cause an unsightly turbid discolored water. Well strainers become clogged so as to prevent proper yield of water.

Microscopic organisms apparently do not affect the health. Possibly the taste and odor at times produce nausea or distaste for food. It would take 12,000 units of *Asterionella* per cubic centimeter to add a milligram of solid matter to a glass of water.

### Sampling for Analysis

In sampling water for microscopical analysis precautions should be taken that the sample be representative and fresh. Water from a tap should be allowed to run to avoid heated stagnant water. Samples from a pond or reservoir should not contain surface scum nor littoral growths. Deep samples are best taken by the method usually employed for dissolved oxygen samples. A quart bottle is fastened by clamps to the side of a two-quart bottle in a water sampler. The bottles are fitted with two-hole rubber stoppers. Glass tubing is arranged as follows: A straight tube, projecting slightly above the stopper, extends to the bottom of the quart bottle. A bent tube is made flush with the underside of the same stopper and connected by a short piece of stiff rubber tubing to a bent glass tube extending through the stopper of the two-quart bottle to its bottom. A straight tube, flush with the underside of the stopper of the two-quart bottle, extends above the stopper from eight to ten inches in order to make a difference of head between the inlet and outlet tubes. The bottles are lowered quickly to the required depth by a marked and measured rope. Watch is kept for bubbles of air which rise to the surface of the water,

sometimes several feet away, until bubbling ceases, which usually takes two minutes. Both bottles must be completely filled before raising, otherwise the sample may be from some other depth than that desired. The water enters the small bottle first and, as it only takes one half minute to lower the apparatus to the desired depth and two minutes for both bottles to fill, the smaller bottle is filled with the last water to enter which is from the desired depth. If the large bottle were not completely filled, the bottles would be filling while being drawn up and the water of the small bottle would represent some unknown depth.

### Sedgwick-Rafter Method of Examination

#### Apparatus Required

A microscope (not necessarily high priced).

Eyeieces—One inch (25 mm.) and one half inch (12 mm.).

Objective—Two thirds inch (16 mm.) and one sixth inch (4 mm.).

Ocular micrometer—Fitted to one-inch eyepiece.

This is ruled with a square of such size that used with a one-inch eyepiece and two-thirds inch objective the tube length of microscope may be adjusted so that the area viewed on the stage will be one square millimeter. The tube length is adjusted by making the square in the eyepiece coincide with a stage micrometer. The large square is usually divided into quarters, one quarter into 25 small squares and one of the latter into 25 tiny squares; each of the last represents a unit of measurement, 400 square microns (20 microns to the side). A micron equals .001 mm.

A stage micrometer—graduated usually to tenths of a millimeter.

Sedgwick-Rafter Counting Cell—a thick slide to which is cemented a brass rim with internal dimensions of length 50 mm., width 20 mm., and depth 1 mm. It has an area of 1,000 square millimeters and a capacity of 1 cubic centimeter. Its depth only must be exact. Several should be provided.

Thin cover glasses, 55 mm. by 25 mm., to use as covers for the cells.

One cubic centimeter pipettes (regular bacteria pipettes will do).

Five cubic centimeter pipettes, volumetric.

A small glass jar of distilled water—for rinsing cells and coverglasses.

Lintless cloth or handkerchiefs—for drying cells and coverglasses.

One-inch test tubes of heavy glass (bacteria dilution tubes).

Five-eighths-inch test tubes of heavy glass (bacteria media tubes).

Sedgwick-Rafter funnels. These are cylindrical, 2-inch diameter, sloping toward the bottom to a neck of  $\frac{1}{2}$ -inch diameter. The distance from top to slope is 9 inches, length of slope 3 inches, length to bottom  $2\frac{1}{2}$  inches.

A small glass jar of distilled water—to furnish water for concentrates.

Perforated rubber stoppers—to fit one half inch tube of funnel.

Silk bolting cloth No. 20.

Steel punch—to make  $\frac{1}{4}$ " diameter discs of bolting cloth for rubber stoppers.

White sand, 60 to 120 mesh, i.e., passing a sieve of 60 mesh to the inch and retained on 120 mesh (Berkshire sand or ground quartz).

Support for battery of funnels.

A small wooden mustard spoon—to measure sand.

Volumetric flasks, 200 cc. capacity.

Test-tube racks.

Record books designed for microscopic examinations.

For field work, which is sometimes of importance due to destruction of organisms in transit, a folding microscope and a metal sling filter are useful but not necessary.

**Procedure.** The actual procedure of examination is simple. Familiarity with the various species is essential. In the limited space of this chapter it is impossible to picture the thousands of forms that exist. The best working book, containing also plates, is "The Microscopy of Drinking Water" by George C. Whipple. References to other books showing plates will be found at the end of the chapter.

Moisten the small end of rubber stopper with water so as to easily pick up a disc of silk bolting cloth from the table and insert tightly into the funnel. Fill the mustard spoon with prepared sand and drop into funnel making one-half inch layer. Pour in 200 cc. of the water to be examined from a flask and allow to filter, thus concentrating the organisms upon the sand. Do not allow the sand to stand until drained dry. Slight suction may be carefully applied to clogged filters. Remove funnel, hold in a slanting position and carefully remove stopper and insert the end of funnel into a one-inch test tube. Wash sand and contents into the test tube by 5 cc. of distilled water, running the latter quickly around the sides of the funnel. Shake water and sand, settle a few moments and decant liquid into the smaller ( $\frac{1}{2}$  inch) test tube. A rack of these concentrates may be prepared at one time for examination. Rinse three or four Sedgwick-Rafter cells and coverglasses in distilled water and carefully dry with lintless cloth. Place coverglasses slantingly across cell so as to leave air space at diagonally opposite ends. Run 1 cc. of concentrate into one corner of cell, air leaving at the opposite corner, and slide coverglass into position to close cell. Allow cells to stand at least five minutes before examining so that organisms will have an opportunity to settle completely, as most of them will. This step is very important. While examination is being made of one cell, others will be settling. Thus at least three should be kept going in rotation when many samples are to be examined.

Examine under the microscope with one-inch ocular containing micrometer and  $\frac{1}{2}$ -inch objective and proper tube length as previously determined. Estimate the number of standard units of each organism present in an entire field within the large square of the eyepiece and note on record sheet. Area only is taken into account. Forms like *Asterionella*, *Diatoma*, *Synedra*, *Tabellaria* may be counted and multiplied by a factor to get the number of units—thus each arm of *Asterionella* may be estimated as equal to one half unit. Filamentous forms like *Melosira*, *Anabaena*, *Aphanizomenon*, *Oscillaria* may be counted in lengths of five units (one-tenth of side of large square) and the total length divided by the number of filaments laid side by side that it would take to measure five units. The quotient multiplied by 25 gives the number of units in the field. *Synedra* in "fine-tooth-comb form," *Fragillaria*, *Urolena*, *Synura* and bulky forms may be quickly compared with a 25-unit square and the number of units in the field estimated. The above method of estimating units is quicker than it reads and tends to eliminate largely the personal element from the count. After the bottom of the slide has been counted, focus should be changed to the top layer and Cyanophyceae, which float, estimated, that is *Anabaena*, *Aphanizomenon*, *Clathrocystis*, *Microcystis*, *Coelosphaerium*, etc.

Standard Methods of the American Public Health Association require 20 fields of the 1000 to be examined. In ordinary practice, however, a careful count of five representative fields is sufficient, choosing fields through the middle of the cell at each end, the center and half way between. After counting, a search of the cell, particularly the edges, is made for missed forms, especially Crustacea which swim to the edges to get air and Protozoa like *Urolena*. The latter are frequently rolling around in the body of the cell. *Anabaena*, *Urolena* and *Dinobryon* commonly break up and disintegrate in the absence of air and must be recognized in such condition. The process of disintegration frequently may be witnessed under the microscope. Sometimes disintegration occurs in transit.

On the record sheet, the amounts of units of each organism are summed up or the number of fields examined and multiplied by a factor to find the total units as referred to the original water. The latter amounts are summed to find the total units of organisms per cubic centimeter.

If the quantities recommended in this chapter are used the factor is found as follows:

The ratio of total cell to counted fields is  $\frac{1000}{5} = 200$ .

The concentration is  $\frac{200 \text{ cc.}}{5 \text{ cc.}} = 40$ .

The final factor is then  $\frac{200}{40} = 5$ .



FIG. 172.—Collection Apparatus for Bacteriological Samples.

Large crustacea found only around the edges and not distributed through the cell should have their total units divided by the concentration rather than multiplied by the factor in referring the count to the original water.

In addition to the count an examination of the original sample in the bottle by naked eye is often useful in detecting such forms as *Uroglana*, *Cyclops*, etc., and in forming a general estimate of the amounts of organisms present.

Many errors may enter into the quantitative estimation of microscopic organisms. The sample bottle should be inverted to distribute the forms, as some float and others settle. Organisms may adhere to the sides of the funnel or to the sand. Others may pass through the sand and some may disintegrate. One of the greatest errors is caused by uneven distribution through the cell when organisms are not numerous. Whipple states that the total error does not usually exceed ten per cent. The author of this chapter believes this figure is too conservative and unavoidably so owing to the large personal element. However results are usually comparative at any one laboratory.



## Tabular Outline Identification of Forms

Sample..... Date of Collection..... Number.....  
 Examined by..... Date of Examination..... Concentration.....

No. of Squares	1	2	3	4	5	6	7	8	9	10	Total	Standard Units Per C.C.
DIATOMACEAE:												
<i>Asterionella</i> ..		1	2		1						4	20
<i>Cyclotella</i> ....												
<i>Diatoma</i> ....												
<i>Fragilaria</i>												
<i>Melosira</i> ...	3	5	4	10	2						24	120
<i>Navicula</i> ..												
<i>Stephanodiscus</i> ..	1	1	1	1	1						5	25
<i>Synedra</i> ....		20		5							25	125
<i>Tabellaria</i> ...					4						4	20

## List of Organisms

## CHLOROPHYCEAE:

*Closterium*  
*Conferva*  
*Eudorina*  
*Paulorina*  
*Pediastrum*  
*Protopoccus*  
*Scenedesmus*  
*Spirogyra*  
*Staurastrum*

## CYANOPHYCEAE:

*Anabaena*  
*Aphanizomenon*  
*Clathrocystis*  
*Coelosphaerium*  
*Microcystis*  
*Oscillaria*

## SCHIZOMYCETES, ETC.:

*Crenothrix*  
*Mold Hyphae*

## PROTOZOA:

*Ceratium*  
*Dinobryon*  
*Glenodinium*  
*Mallomonas*  
*Peridinium*  
*Synura*  
*Trachelomonas*  
*Uroglena*  
*Vorticella*

## ROTIFERA:

*Anuraea*  
*Polyarthra*  
*Synchaeta*

## CRUSTACEA:

*Bosmina*  
*Cyclops*  
*Daphnia*

## OTHER ORGANISMS:

*Anguillula*  
*Acarina*

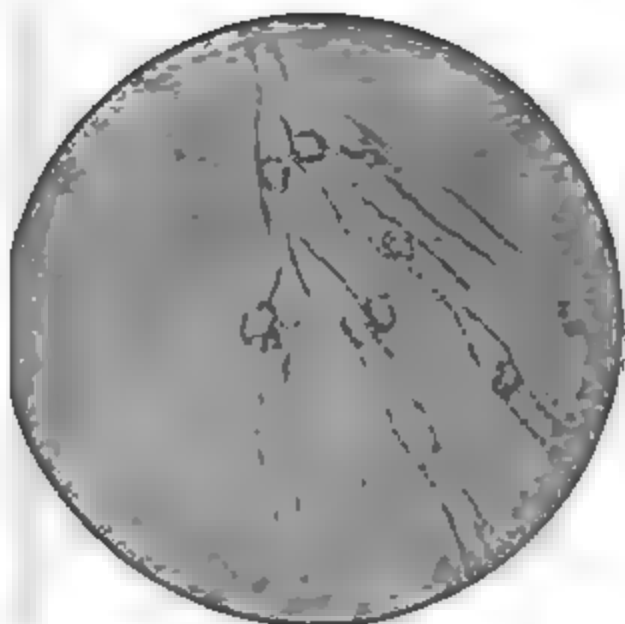
## TOTAL ORGANISMS:

Amorphous Matter  
 Miscellaneous Bodies  
 Sponge Spicules

Amorphous matter comprises organic debris due largely to broken-down microscopic organisms and zoöglea.<sup>1</sup> It is usually of little importance but in connection with consumption of dissolved oxygen in reservoirs just below the thermocline and at the bottom it has been shown to have importance.<sup>2</sup>

<sup>1</sup> The estimation should not include mineral matter, silt, precipitated iron, etc., as indicated in the last edition of "Standard Methods of the American Public Health Association," since this can serve no apparently good purpose. Neither is such standard in agreement with Whipple.

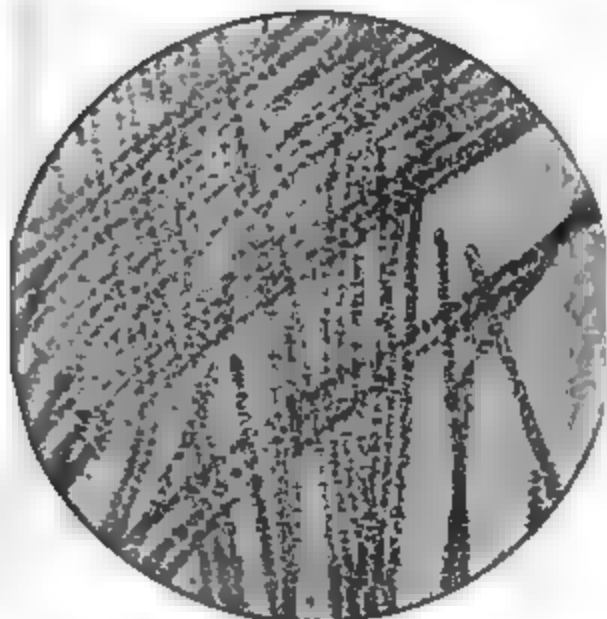
<sup>2</sup> "Thermocline Studies at Kensico Reservoir," Hale and Dowd, Jour. Ind. Eng. Chem., Vol. 9, page 81.



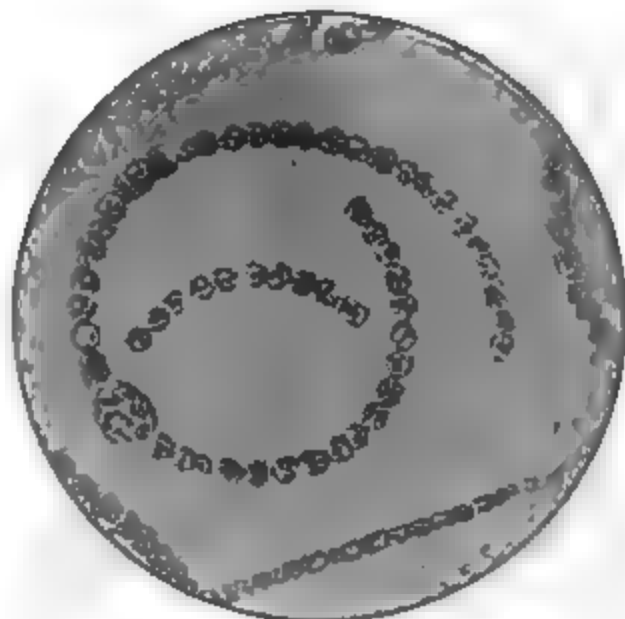
1. *Dinobryon*, magnification 250.



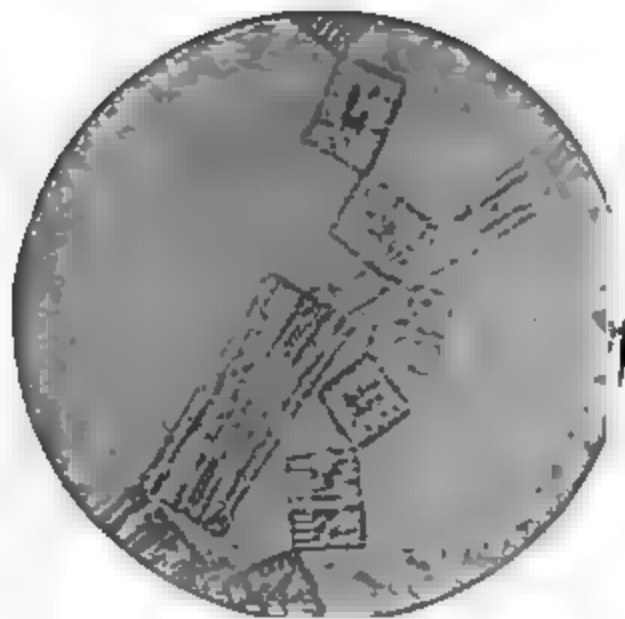
2. *Clathrocystis*, magnification 250.



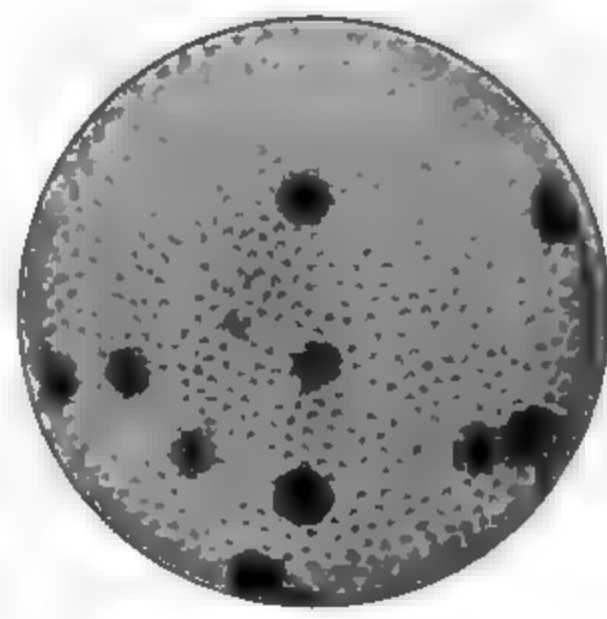
3. *Aphanizomenon*, magnification 250.



4. *Anabaena*, magnification 250.



5. *Tabellaria*, magnification 250.

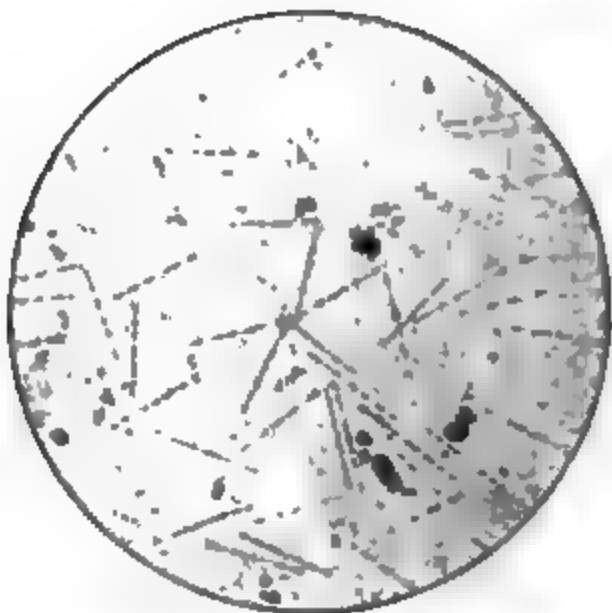


6. *Volvox*, magnification 100.

2, 3, 4. grassy to pig-pen odor.

5. Aromatic geranium to fishy odor.

1, 6. Fishy odor.

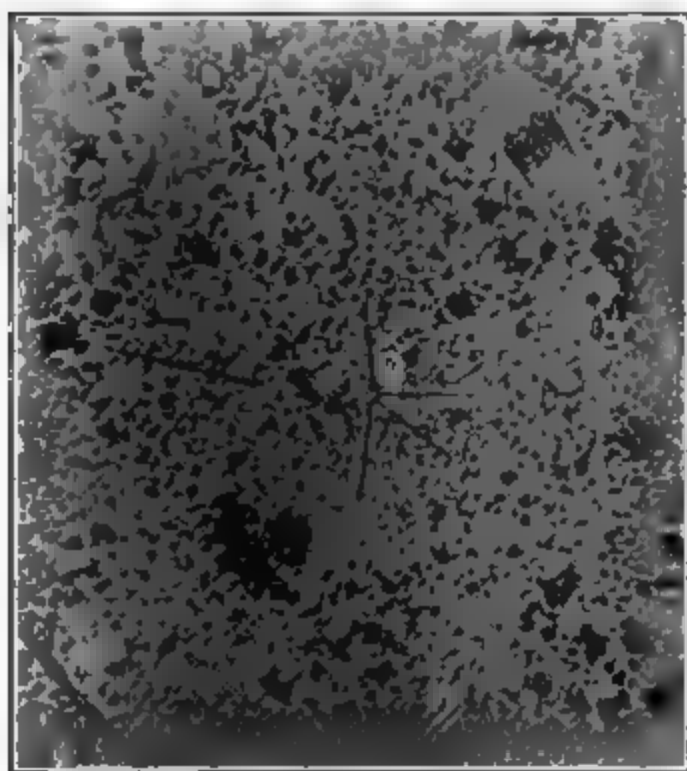


*A*

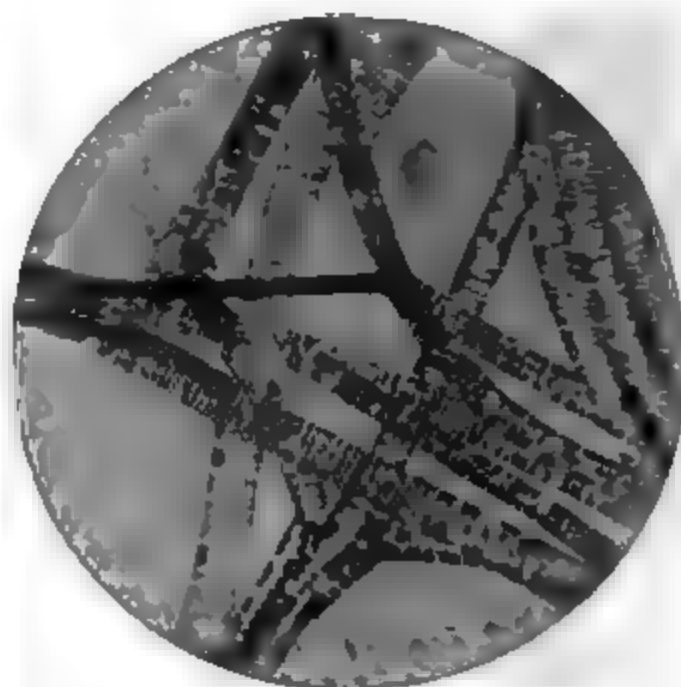


*B*

Asterionella before (*A*) and after (*B*) treatment with copper sulphate, 1/5 p.p.m. Note effect upon coloring matter. Magnification 150. Causes geranium to fishy odor.



Water concentrate as it appears under the microscope. 1. Synedra, fine tooth comb. 2. Synedra, needle-form. 3. Asterionella. 4. Melosira.



*Fragilaria*, magnification 150.



*Ulothrix*, magnification 75.

**Identification of Forms.** On page 1448 is shown a section from a page of the record book used in New York City's Water Department Laboratories, showing the classification of organisms and the commoner forms found.

As the magnification used for counting is only 87 one must learn to identify the forms quickly at that magnification. Occasionally it is necessary to use the one-half-inch ocular to make certain the identification, the latter magnification being 146. Young forms frequently differ from mature forms and confusion arises. It may be helpful to mention certain distinguishing features for some of these commoner forms, avoiding so far as possible technical terms.

*Asterionella* (little star) in its usual form is readily recognized. Four to eight arms connected at one end, slightly larger than the other end, and radiating from the attached ends suggest its name. The arms are usually more slender near the center in girdle view. The coloring matter appears as regularly spaced dots or dashes strung along the arm in single row. There is another form of *Asterionella* in which the arms attach at either end in zig-zag manner with occasionally four arms arranged in star fashion. This form may be confused with "*Diatoma*" or "*Tabellaria*," but may be distinguished by the appearance of individual arms in valve view, *Diatoma* having cross striations and *Tabellaria* an oval outlined in a swollen center.

It may be mentioned that Diatoms have two valves fitting together like clams, oysters or scallops but different in that they overlap like the cover and bottom of a petri dish or a pill box. The valve view is that of the top of the box and girdle view that of the edge. (Different authors use different terms. The above is according to Whipple.)

*Diatoma* in girdle view has straight sides and square ends, joining at the corners to form zig-zag chains. The valve view is distinctive from *Asterionella* and from *Tabellaria*; it has cross striations.

*Tabellaria* usually has wider arms than *Asterionella* or *Diatoma* and two well-defined parallel marks or lines extending from each end nearly to the middle. In some forms these are missing. The arms join in zig-zag fashion with sometimes three or four in star shape. As mentioned before the valve view is distinctive, being swollen and marked with an oval at the center. There is also a distinctive short chubby form.

*Synedra* in common form looks like a fine-tooth comb, the needle-like individuals being attached side by side at the center forming a serrated edge. The edge distinguishes it from *Fragillaria* which also forms masses side by side but the ends of the latter are square with no appearance of teeth. Sometimes *Synedra* exists only in individual short needles and again in very long needles.

*Meridion* also joins side by side but being wider at one end than the other forms disc-like patterns. The valve view is also distinctive, like a base-ball club and striated cross-wise.

*Gomphonema* is also wedge-shaped like *Meridion* but does not join in masses and in valve view is shaped like a rolling pin. It has a pedicle which is frequently missing.

Many forms, once seen, are very readily distinguished, *Stauroneis* like an elongated diamond with a cross marked from corner to corner, *Pleurosigma*, with a double curve reminding one slightly of the letter "S," *Navicula*, shaped like a little boat, *Melosira*, with its cylindrical cells joined end to end to form filaments containing considerable coloring matter. *Cyclotella* appears usually as small perfect circles without contents whereas *Stephanodiscus* is a larger

circle with coloring matter conspicuous and sometimes concentric markings visible on the circumference. On edge a view as of a pill box is often obtainable.

The coloring matter of the *Diatoms* may appear from yellow to brown but often a mere black and white effect without much suggestion of color.

The Chlorophyceae (green growth) have green coloring matter. The common forms are readily distinguished and remembered from illustrations. *Dictyosphaerium* and *Dimorphococcus* are similar small coccus-like forms joined by spider-like threads together, the former from a concave side, the latter from a convex side. *Pandorina* and *Eudorina* are coccus-like forms set in a jelly ball, the former with the coccus bodies grouped together closely at the center, the latter with them separated and spaced regularly near the surface. *Volvox* is a large revolving jelly-like hollow ball with the surface dotted with coccus forms and similar to *Uroglena* of the Protozoa, but differs in containing several conspicuous larger green cells which are in reality young Volvocea.

The Cyanophyceae (blue growth) contain a blue-green coloring matter. *Anabaena* appears like a string of beads. It differs from *Nostoc* in not having a gelatinous sheath, from *Sphaerozyga* in that its spores and heterocysts are not adjacent whereas in the latter a heterocyst is between two spores. The spores are larger than the vegetative cells. It differs from *Cylindrospermum* in that the latter has its heterocysts terminal with large spore adjacent, and the latter filament is sometimes tapering.

*Aphanizomenon* under high power has a beaded appearance and contains a very long oval spore which is scarce. Under the ordinary power *Aphanizomenon* appears like a pencil mark on drawing paper and frequently appears in attached masses of filaments.

*Oscillaria* is a pale blueish filament of even color without granulation, with rounded ends, straight sides (i.e., no beaded appearance) and cross striations. At times it may be seen to oscillate or wave back and forth (hence its name).

Of the Schizomycetes, *Crenothrix* is fairly common and occurs in well waters containing iron or manganese. It occurs as dark brown masses due to discoloration with iron or manganese. The latter may be dissolved by acid when the oblong cells become visible embedded in a gelatinous sheath, but not touching each other, and forming a filament. *Anthophyza* pedicles, a Protozoan, are sometimes mistaken for it but the latter is usually branched like a "Y" and has longitudinal striations.

The Protozoa are the lowest forms of animal life, unicellular in structure, though they may aggregate in colonies. Of *Dinobryon* frequently only the pencil-like outlines of the tiny cups or trumpet-like shells are visible (and difficultly seen), one set in another, to form branching aggregations. The spores of *Dinobryon* are sometimes mistaken for *Cyclotella*. *Glenodinium* and *Peridinium* are oval and each has a groove across the center. The former is smaller and has a smoother outline than the latter. *Synura* is a small moving yellowish ball of oval animalcules joined concentrically and closely packed. *Uroglena* is a large jelly-like hollow ball of minute animalcules, the latter embedded near the surface, similar in appearance to *Volvox*, as previously mentioned, but lacking the large green cells. It rolls around slowly in the center of the liquid of the cell. Broken pieces have the shape of a piece of a rubber ball. It is visible to the naked eye and recognizable in the bottle.

Rotifera, Crustacea, etc. (more complicated animal forms) are readily distinguished from their pictures in most instances. Many are visible to the

naked eye. *Cyclops* may readily be recognized in the bottle by its shape and swift darting motion. It appears about the size of a pin head shaped somewhat like a tiny fish, but wider in proportion. *Bosmina* (little cow) and *Acarina* (little spider) each have a peculiar jerky motion of their own.

### Control of Microscopic Organisms

Troublesome microscopic growths are controlled as follows:—Reservoirs are shut off from the service and bypassed until the forms die out under storage which may take three weeks to three months. Aeration by fountains will disintegrate certain fragile forms like *Uroglena*, *Anabaena*, even *Asterionella* and assist in removing odors. It has lately been shown that *Crenothrix* may be controlled by chloramine or liquid chlorine (Montfort & Barnes). But the method of widest application is that of Moore & Kellerman, the application of copper sulphate in dosage ranging from .05 to 1.00 parts per million by weight according to the particular species (or even varieties) of microscopic organisms present. The chemical has been usually applied by rowing around in boats dragging burlap bags, containing, usually, fifty pounds each, through the surface of the water, allowing wind, wave and diffusion to mix the treated water with the remainder.

New York City has demonstrated, very satisfactorily, that dry feed of the chemical by automatic accurate electrical apparatus to the water flowing in an aqueduct a short time before entering the reservoir is absolutely feasible and successful even at winter temperatures and with ice-covered reservoirs. The feed is by means of a slowly moving shutter fed from a hopper. The copper sulphate drops into a screen revolved by the water in a narrowed portion of the aqueduct. The metal parts of the apparatus should be made of copper to prevent corrosion. A dosage of 0.2 parts per million destroyed *Asterionella* and under such circumstances the killing dosage is accurately known.

The effect of treatment of microscopic organisms by copper sulphate is shown by an immediate intensification of distinctive odors, by reduction of the number of organisms in the water through sedimentation, by the appearance of the organisms under the microscope—the coloring matter being knocked to pieces, so to speak. Sometimes there is an increase in the water bacteria which feed upon the decayed organisms. The Cyanophyceae may produce scum after treatment which is of varied colors, pale blue, yellow, red or brown.

Sometimes fish are killed by the treatment but this is more apt to occur from smothering due to clogging of the gills with dead organisms or reduction of oxygen by the dead organisms. It is only occasionally that fish are killed in quantities, even though larger doses are usually applied than shown in the following table calculated from data published by Moore & Kellerman:

**Killing Dosage of Copper Sulphate for Fish**

Fish	Parts per Million	Pounds per Million Gallons (Approximate)
Trout.....	0.14	1.2
Carp.....	0.33	2.8
Suckers.....	0.33	2.8
Catfish.....	0.40	3.5
Pickrel.....	0.40	3.5
Goldfish.....	0.50	4.0
Perch.....	0.67	5.5
Sunfish.....	1.33	11.1
Black Bass.....	2.00	16.6

Experience differs with waters of different composition and with temperature as to the right dosage to apply for each organism. It is believed that it is a waste of copper sulphate to apply an insufficient quantity. When the correct quantity is applied the water is usually cleared within three to four days. The following table is made up from data furnished by Moore & Kellerman, Whipple, various other sources and personal experience. The latter are starred.

### Copper Sulphate Required for Treatment of Different Species

Organisms	Parts per Million	Pounds per Million Gallons
<b>DIATOMACEAE:</b>		
<i>Asterionella</i> .....	0.20*	1.7
<i>Fragilaria</i> .....	0.25	2.1
<i>Melosira</i> .....	0.33	2.8
<i>Navicula</i> .....	0.07	0.6
<i>Synedra</i> .....	0.50*	4.2
<i>Tabellaria</i> .....	0.50*	4.2
<b>CHLOROPHYCEAE:</b>		
<i>Cladophora</i> .....	0.50	4.2
<i>Closterium</i> .....	0.17	1.4
<i>Coelastrum</i> .....	0.33	2.8
<i>Conjerva</i> .....	0.25	2.1
<i>Desmidium</i> .....	2.00	16.6
<i>Draparnaldia</i> .....	0.33	2.8
<i>Eudorina</i> .....	10.00	83.0
<i>Hydrodictyon</i> .....	0.10	0.8
<i>Microspora</i> .....	0.40	3.3
<i>Palmella</i> .....	2.00	16.6
<i>Pandorina</i> .....	10.00	83.0
<i>Raphidium</i> .....	1.00	8.3
<i>Scenedesmus</i> .....	1.00	8.3
<i>Spirogyra</i> .....	0.12	1.0
<i>Staurastrum</i> .....	1.50	12.5
<i>Ulothrix</i> .....	0.20*	1.7
<i>Volvox</i> .....	0.25	2.1
<i>Zygnema</i> .....	0.50	4.2
<b>CYANOPHYCEAE:</b>		
<i>Anabaena</i> .....	0.12*	1.0
<i>Aphanizomenon</i> .....	0.50*	4.2
<i>Clathrocystis</i> .....	0.12*	1.0
<i>Coelosphaerium</i> .....	0.33	2.8
<i>Microcystis</i> .....	0.20	1.7
<i>Oscillaria</i> .....	0.50*	4.2
<b>PROTOZOA:</b>		
<i>Chlamydomonas</i> .....	0.50	4.2
<i>Cryptomonas</i> .....	0.50	4.2
<i>Dinobryon</i> .....	0.33	2.8
<i>Euglena</i> .....	0.50	4.2
<i>Glenodinium</i> .....	0.50	4.2
<i>Mallomonas</i> .....	0.50	4.2
<i>Peridinium</i> .....	2.00	16.6
<i>Synura</i> .....	0.20*	1.7
<i>Uroglena</i> .....	0.10*	0.8
<b>SCHIZOMYCETES:</b>		
<i>Beggiatoa</i> .....	5.00	41.5
<i>Cladothrix</i> .....	0.20	1.7
<i>Crenothrix</i> .....	0.33	2.8
<i>Leptomitua</i> .....	0.40	3.3

The following illustration shows the corner of a bacteriological laboratory for the sanitary examination of water.

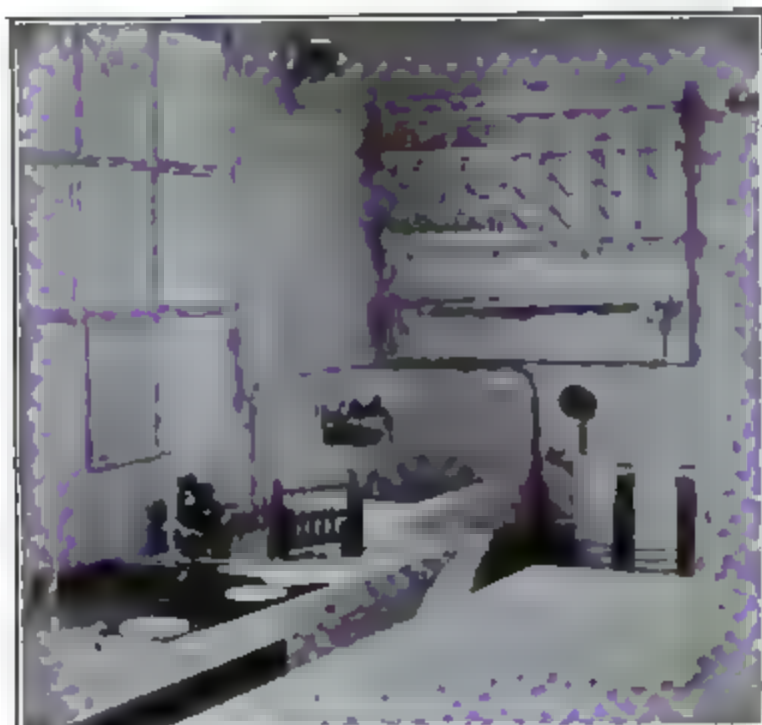


FIG. 173. Microscopical Apparatus, Catskill Laboratory, Ashokan, N. Y.

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## BACTERIOLOGICAL EXAMINATION OF WATER

FRANK E. HALE

The routine bacteriological examination is essentially simple. It consists of obtaining empirically the total number of bacteria under certain standard conditions and of testing for the intestinal group, *B. coli*. Usually only under special conditions is search made for specific disease bacteria which may be carried by water supply, such as *Bacillus typhi*, *Bacillus paratyphi*—A and B, *Spirillum cholerae*, *Bacillus dysenteriae*—various types, *Bacillus anthracis*, etc.

## Sampling

Samples must be taken in dry-sterilized bottles, with well-ground glass stoppers. Two ounce capacity is usually sufficient for routine tests. The bottles are preferably protected by covering the stoppers and necks with tinfoil and further protected by placing in a metal screw-top can (two inch by four inch). It is frequently convenient to use quart bottles steam-sterilized at fifteen pounds pressure, and capped with tinfoil, when special samples are to be brought in by hand,—the same sample serving for the physical, microscopical and chemical analyses after making the bacteriological examination. Such samples transported in leather bags of proper size do not change temperature

more than a few degrees in several hours on the hottest days though not protected by ice. For the two-ounce bottles special aluminum cases, holding small quantities of ice and fitting the bags, are light and convenient. For shipping, the small bottles may be packed in a copper-lined wooden box containing a receptacle for the bottles and space for ice below.



FIG. 174. Sampling Apparatus for Deep Samples.

In sampling care must be taken to take representative samples, avoiding contamination and avoiding stagnant water. Temperature is often a guide but it must be taken from the source or in a separate bottle with the thermometer bulb immersed in the water a few minutes before reading. Allow tap samples to run thoroughly, particularly in warm boiler rooms. Handle sterilized bottles by the bottom and keep fingers away from the necks. Handle stoppers with the tinfoil in place. Avoid splashing or over-running bottles. In streams plunge bottle below the surface and sample by swinging hand up-stream with mouth of bottle pointed up-stream so as to avoid water washing over the hand into bottle. Similarly in a reservoir, swing the mouth of the bottle forward while filling. Do not rinse a sterilized bottle. These rather minute directions are given because in a long experience they have

frequently been found necessary. Experts do not always take the samples though the value of their work depends upon the care with which the samples are taken. Men have even been caught reading thermometers after drawing them up twenty feet from the surface of a reservoir.

## BACTERIOLOGICAL EXAMINATION OF WATER 1455

Samples from a depth in a reservoir are best taken if possible from an effluent pipe when regular draft is from a depth. In other cases sterilized bottles may be lowered to the required depth and stoppers pulled out by means of special samplers. In many cases it has been found satisfactory to take them by the two-bottle method as used for dissolved oxygen and described under "Microscopic Examination of Water." In this case the quart bottle should be thoroughly cleaned, handled as little as possible, and the water poured into a bacteria bottle after drawing to the surface. The quart bottle is pretty thoroughly rinsed during the process of sampling.

Samples should be tested the same day they are collected, preferably within a few hours. Expressed and iced samples will probably give a fairly reliable index of *B. coli* content but cannot be relied on for total counts.

### Apparatus and Materials Needed

Bacteria bottles—two-ounce glass-stoppered (well ground).  
Metallic containers for above, screw-cap, two inch by four inch.  
Tinfoil, four inch wide, in rolls for capping.  
Bacteria certificates for sample data.  
Containers for carrying samples—leather bags with aluminum ice cases to fit.  
Containers for shipping samples—copper-lined ice chests.  
Dry-sterilizer for bottles and pipettes, to operate at 170° C.  
Autoclave to operate at 15 pounds steam pressure, sterilization of media.  
1 cc. pipettes with two marks and also conveniently graduated to show 0.1 cc. above the upper 1 cc. mark.  
10 cc. pipettes, preferably straight tube pipettes with graduation also for 5 cc. and 9 cc.  
Pipette boxes for sterilized pipettes, 3½" square by 14" long.  
Dilution test tubes, 1" diameter, medium weight.  
Media test tubes, ½" diameter, heavy weight, not lipped.  
Dilution flasks, Erlenmeyer, 16-ounce capacity, for sterilized water.  
Flasks, ½ liter, 1 liter, etc., for media preparation and bulk storage.  
Test tube racks for dilution tubes.  
Wire cages for media tubes, 4" by 5" by 5½" high.  
Non-absorbent cotton for plugging tubes.  
Footless Smith tubes for *B. coli* tests, or small test tubes inverted in large test tubes for same capacity in either case four times the amount of water to be tested.  
Metal racks for Smith tubes.  
Agateware double boilers for making media.  
Agateware kettles for making media.  
Agateware funnels, 6 inch, for filtering media.  
Cotton flannel for filtering media.  
Large beakers for making media.  
Earthenware pitchers for filling tubes with media.  
Side-neck burettes for filling tubes with media (side neck connected to funnel of media).  
Apparatus for keeping media warm while filtering.  
Gas stoves for heating media.  
Petri dishes, 10 cm. diameter and flat bottomed, with both glass covers (20° C. incubation) and porous covers (37° C. incubation).  
Agateware sauce pans for melting media in tubes before planting.  
20° C. incubator with thermometer, automatic regulator and safety burner.  
37° C. incubator with thermometer, automatic regulator and safety burner.  
(In many laboratories the incubators are now electrically operated.)  
Burner for flaming tubes before planting.  
Counting stand with engraved lines to assist in counting.  
Engraver's lens for counting, B. & L. 146, magnification 2½ diameters, 3½ X.  
Tallying register for counting.  
Balance, similar to an apothecary's, for quick weighing.  
Balance, analytical beam type, for accurate weighing.  
Record books for bacteriological results.

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Microscope with condenser and assortment of lenses: at least  $\frac{1}{4}$ ",  $\frac{1}{2}$ " and 1" eyepieces and  $\frac{1}{4}$ ",  $\frac{1}{2}$ " and  $\frac{1}{12}$ " objectives. (Satisfactory hanging drops may be made with  $\frac{1}{4}$ " eyepiece and  $\frac{1}{2}$ " objective. The  $\frac{1}{12}$ " is used only in oil immersion with condenser.)

Slides, plain and concaved (latter for hanging drops).

Cover slips, round or square.

Platinum needles with holders for transferring cultures.

Cleaning mixture for cleaning glassware.

Distilled water for preparation of all culture media and reagents.

Meat extract; Liebig's is Standard.

Peptone; Witte's is Standard (N. Y. City Water Department Laboratories have found Digestive Ferments Company's reliable and just as satisfactory if not better. Some laboratories have found Armour's and Fairchild's satisfactory).

Lactose and all other sugars the purest obtainable.

Agar. Frequently needs soaking in water and draining before use because of salt. Shall be dried  $\frac{1}{2}$  hour at  $105^{\circ}$  C. before weighing.

Gelatine, of light color, containing not more than a trace of arsenic, copper, sulphides, free from preservatives, and of such a melting point that "standard nutrient gelatin" shall not melt below  $25^{\circ}$  C. Gelatin shall be dried  $\frac{1}{2}$  hour at  $105^{\circ}$  C. before weighing.

Litmus—reagent litmus of highest purity (not litmus cubes) or azolitmin (Kahlbaum's).

General chemicals—chemically pure so far as possible.

### Preparation of Culture Media

**Adjustment of Reaction.** (a) Phenol Red Method for adjustment to a hydrogen-ion concentration of  $P_{H+} = 6.8-8.4$ . Withdraw 5 cc. of the medium,



FIG. 175. Bacteriological Apparatus. Fermentation Tubes, Petri Dishes, Pipettes, Culture Media, etc.

dilute with 5 cc. of distilled water, and add 5 drops of a solution of phenol red (phenol sulphone phthalein). This solution is made by dissolving 0.04 grams of phenol red in 30 cc. of alcohol and diluting to 100 cc. with distilled water.

Titrate with a 1 : 10 dilution of a standard solution of NaOH (which need not be of known normality) until the phenol red shows a slight but distinct pink color. Calculate the amount of the standard NaOH solution which must be added to the medium to reach this reaction. After the addition check the reaction by adding 5 drops of phenol red to 5 cc. of the medium and 5 cc. of water.

(b) **Titration with Phenolphthalein.** (For the convenience of those who wish to retain the use of this method for the present it is given here, but it is recommended that as soon as possible the more accurate method of determining the hydrogen-ion concentration be substituted.)

In a white porcelain dish put 5 cc. of the medium to be tested, add 45 cc. of distilled water. Boil briskly for one minute. Add 1 cc. of phenolphthalein solution (5 grams of commercial salt to one liter of 50 per cent alcohol). Titrate immediately with a N/20 solution of sodium hydrate. A faint but distinct pink color marks the true end point. This color may be precisely described as a combination of 25 per cent of red (wave-length approximately 658) with 75 per cent of white as shown by the disks of the standard color top made by the Milton Bradley Educational Co., Springfield, Mass.

All reactions shall be expressed with reference to the phenolphthalein neutral point and shall be stated in percentages of normal acid or alkali solutions required to neutralize them. Alkaline media shall be recorded with a minus (-) sign before the percentages of normal acid needed for their neutralization and acid media with a plus (+) sign before the percentages of normal alkali solution needed for their neutralization.

The standard reaction for culture media for water analysis shall be +1.0 per cent as determined by tests of the sterilized medium. As ordinarily prepared, broth and agar will be found to have a reaction between +0.5 and +1.0. For such media no adjustment shall be made. The reaction of media containing sugar shall be neutral to phenolphthalein. Whenever reactions other than the standard are used, it shall be so stated.

**Sterilization.** All media and dilution water shall be sterilized in the autoclave at 15 lbs. (120° C.) for 15 minutes after the pressure reaches 15 lbs. All air must be forced out of the autoclave before the pressure is allowed to rise. As soon as possible after sterilization the media shall be removed from the autoclave and cooled rapidly. Rapid and immediate cooling of gelatin is imperative.

Media shall be sterilized in small containers, and these must not be closely packed together. No part of the medium shall be more than 2.5 cm. from the outside surface of the glass. All glassware shall be sterilized in the dry oven at 170° C. for at least 1½ hours.

**Nutrient Broth.** *To make one liter:*

1. Add 3 grams of beef extract and 5 grams of peptone to 1,000 cc. of distilled water.
2. Heat slowly on a steam bath to at least 65° C.
3. Make up lost weight and adjust the reaction to a faint pink with phenol red, or if the phenolphthalein titration is used, and the reaction is not already between +0.5 and +1, adjust to +1.
4. Cool to 25° C. and filter through filter paper until clear.
5. Distribute in test-tubes, 10 cc. to each tube.
6. Sterilize in the autoclave at 15 lbs. (120° C.) for 15 minutes after the pressure reaches 15 lbs.

**Sugar Broths:** Sugar broths shall be prepared in the same general manner as nutrient broth with the addition of 0.5% of the required carbohydrate just before sterilization. The removal of muscle sugar is unnecessary as the beef extract and peptone are free from any fermentable carbohydrates. The

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reaction of sugar broths shall be a faint pink with phenol red or, if on titration with phenolphthalein the reaction is not already between neutral and +1, adjust to neutral. Sterilization shall be in the autoclave at 15 pounds (120° C.) for 15 minutes after the pressure reaches 15 pounds, provided the total time of exposure to heat is not more than one-half hour; otherwise a 10 per cent solution of the required carbohydrate shall be made in distilled water and sterilized at 100° C. for 1½ hours, and this solution shall be added to sterile nutrient broth in amount sufficient to make a 0.5 per cent solution of the carbohydrate and the mixture shall then be tubed and sterilized at 100° C. for 30 minutes, or it is permissible to add by means of a sterile pipette directly to a tube of sterile neutral broth enough of the carbohydrate to make the required 0.5 per cent. The tubes so made shall be incubated at 37° C. for 24 hours as a test for sterility.

### **Nutrient Gelatin.** *To make one liter:*

1. Add 3 grams of beef extract and 5 grams of peptone to 1,000 cc. of distilled water and add 100 grams of gelatin dried for one-half hour at 105° C. before weighing.
2. Heat slowly on a steam bath to 65° C. until all gelatin is dissolved.
3. Make up lost weight and adjust the reaction to a faint pink with phenol red, or if the phenolphthalein titration is used, and the reaction is not already between +0.5 and +1, adjust to +1.
4. Filter through cloth and cotton until clear.
5. Distribute in test-tubes, 10 cc. to each tube, or in larger containers as desired.
6. Sterilize in the autoclave at 15 lbs. (120° C.) for 15 minutes after the pressure reaches 15 lbs.

### **Nutrient Agar.** *To make one liter:*

1. Add 3 grams of beef extract, 5 grams of peptone and 12 grams of agar, dried for one-half hour at 105° C. before weighing, to 1,000 cc. of distilled water. Boil over a water bath until all the agar is dissolved, and then make up the loss by evaporation.
2. Cool to 45° C. in a cold water bath, then warm to 65° C. in the same bath, without stirring.
3. Make up lost weight and adjust the reaction to a faint pink with phenol red, or if the phenolphthalein titration is used, and the reaction is not already between +0.5 and +1, adjust to +1.
4. Filter through cloth and cotton until clear.
5. Distribute in test-tubes, 10 cc. to each tube, or in larger containers, as desired.
6. Sterilize in the autoclave at 15 lbs. (120° C.) for 15 minutes after the pressure reaches 15 lbs.

**Litmus or Azolitmin Solution.** The standard litmus solution shall be a 2 per cent aqueous solution of reagent litmus. Powder the litmus, add to the water and boil for five minutes. The solution usually needs no correction in reaction and may be at once distributed in flasks or test-tubes and sterilized as is culture media. It should give a distinctly blue plate when 1 cc. is added to 10 cc. of neutral culture medium in a Petri dish.

## BACTERIOLOGICAL EXAMINATION OF WATER 1459

The standard azolitmin solution shall be a 1 per cent solution of Kahlbaum's azolitmin. Add the azolitmin powder to the water and boil for five minutes. The solution may need to be corrected in reaction by the addition of sodium hydrate solution so that it will be approximately neutral and will give a distinctly blue plate when 1 cc. is added to 10 cc. of neutral culture medium in a Petri dish. It may be distributed in flasks or test-tubes and sterilized as is culture media.

**Litmus-lactose-agar.** Litmus-lactose-agar shall be prepared in the same manner as nutrient agar with the addition of 1 per cent of lactose just before sterilization. The reaction shall be a faint pink with phenol red, or, if on titration with phenolphthalein the reaction is not already between neutral and +1, adjust to neutral. One cc. of sterilized litmus or azolitmin solution shall be added to each 10 cc. of the medium just before it is poured into the Petri dish, or the mixture may be made in the dish itself.

### **Endo's Medium.** *To make one liter:*

1. Add 5 grams of beef extract, 10 grams of peptone and 30 grams of agar dried for one-half hour at 105° C., before weighing, to 1,000 cc. of distilled water. Boil on a water bath until all the agar is dissolved and then make up the loss by evaporation.
2. Cool the mixture to 45° C. in a cold water-bath, then warm to 65° C. in the same bath without stirring.
3. Make up lost weight, titrate and if the reaction is not already between neutral and +1 adjust to neutral.
4. Filter through cloth and cotton until clear.
5. Distribute 100 cc. or larger known quantities in flasks large enough to hold the other ingredients which are to be added later.
6. Sterilize in the autoclave at 15 lbs. (120° C.) for 15 minutes after the pressure reaches 15 lbs.
7. Prepare a 10 per cent solution of basic fuchsin in 95 per cent alcohol, allow to stand 20 hours, decant and filter the supernatant fluid. This is a stock solution.
8. When ready to make plates melt 100 cc. of agar in streaming steam or on a waterbath. Dissolve 1 gram of lactose in 15 cc. of distilled water, using heat if necessary. Dissolve 0.25 gram anhydrous sodium sulphite in 10 cc. of water. To the sulphite solution add 0.5 cc. of the fuchsin stock solution. Add the fuchsin-sulphite solution to the lactose solution and then add the resulting solution to the melted agar. The lactose used must be chemically pure and the sulphite solution must be made up fresh.
9. Pour plates and allow to harden thoroughly in the incubator before use.

(NOTE. The methods for nutrient broth, sugar broths, nutrient gelatin, nutrient agar, and litmus-lactose-agar are given above in that form because they are the present adopted standard methods of the American Public Health Association. It is the opinion of the author that the adoption of Liebig's beef extract for fresh beef infusion and the reduction of the peptone by one-half have too greatly weakened the media. Media made according to the 1912 edition standard methods are still in use in the Water Department Laboratories of New York City.)

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**Brilliant-Green Lactose Peptone Bile.** The composition for approximately one liter is as follows:

Distilled water .....	1,000 grams.
Oxgall (desiccated fresh entire bile) .....	50 "
Peptone .....	10 "
Lactose .....	10 "
Brilliant Green .....	0.1 "

1. Heat 1 liter of distilled water in double boiler until water in outer vessel boils.
2. Add 50 grams of dried oxgall and 10 grams of peptone stirring until all ingredients are dissolved.
3. Continue boiling for one hour.
4. Remove from flame and add 10 grams of powdered lactose.
5. Filter through cotton flannel until clear.
6. To each liter of the filtrate add 10 cc. of a 1 per cent solution of brilliant-green.
7. Tube and sterilize in autoclave for 15 minutes at 15 lbs. pressure. Satisfactory results have been obtained with different brands and different samples of the dye obtained from Bayer & Co., Leitz & Co., and Merck & Co., all of New York City.

**Hesse Agar.** The composition for approximately 1 liter is as follows:

Agar (dried) .....	4.5 grams.
Peptone .....	10. "
Beef extract, Liebig's .....	5. "
Salt (sodium chloride) .....	8.5 "
Distilled water .....	1,000. "

Dissolve 4.5 grams of dry agar in 500 cc. distilled water by heating over a free flame, making up loss in weight by evaporation. Into another vessel 500 cc. of distilled water is poured and to this is added 10 grams of peptone, 5 grams of Liebig's beef extract, and 8.5 grams of salt. This is heated until all is dissolved and the loss in weight by evaporation is made up by adding distilled water.

Add the two solutions together; boil 30 minutes; make up loss in weight with distilled water, filter through absorbent cotton held in the funnel by cotton flannel, passing the filtrate through several times until perfectly clear. Test the reaction; adjust, if necessary, to +1.0, and tube, using 10 cc. in each tube. Sterilize for 15 minutes at 15 lbs. pressure in an autoclave. Cool with running tap water and store in an ice-chest, the air of which is saturated with moisture.

**Russell Media.** To ordinary extract agar adjusted neutral to litmus add 1 per cent of lactose and 0.1 per cent of glucose and sufficient litmus to give a good color. Tube and slant leaving a generous "butt" at bottom of tube for stab inoculation.

### Examination of Water for Total Bacteria

The gelatine count is more particularly useful in connection with determining the efficiency of filter plants, since the counts are higher than the agar counts (averaging usually about ten times as high) and in examination of well waters by indication of surface contamination through the presence of liquifiers.

In plating with gelatine media it is usually necessary to use 0.1 cc., or less as well as 1 cc., in order to obtain the right amount of colonies on a plate. Standard methods require planting in duplicate.

Melt tubes of nutrient gelatine or nutrient agar in boiling water,—the latter needs thorough boiling for several minutes to entirely soften. Let cool until luke-warm, just barely warm to the touch. Shake the sample of water vigorously and introduce 1 cc. or less into the bottom of a petri-dish lifting the cover on one side but not removing from over the bottom. The quantity of water used should of course be accurately measured. Be careful not to contaminate the pipette by touching to anything other than the inside bottom of the petri-dish. Use glass-covered petri-dishes for incubation at 20° C. and porous covers for 37° C., in order to overcome spreaders at the higher temperature. Remove a tube of the media from the warm water, dry with a towel, remove the cotton plug, flame the open end of tube and pour into petri-dish. Carefully rotate dish to mix the media with the water and set on a level plate to harden. Agar hardens so quickly that it must be handled and mixed expeditiously. Incubate gelatine plates at 20° C. and agar plates at 37° C.

The gelatine plates are counted after 48 hours and the agar plates after 24 hours.

Each minute bacillus must grow where caught in the solid medium and after sufficient time forms a colony large enough to be seen with the naked eye. Many are however very tiny, so that a hand lens magnifying two and one-half diameters is used in counting. A tallying machine is used to keep count, one tally being made for every three colonies usually, to assist the speed of counting. For accuracy there should be 25 to 250 colonies on a plate, unless less than 25 grew from 1 cc. Fictitious accuracy should be avoided. The following table should be followed in recording results:

Number of bacteria per cc.

From	1 to	50 shall be recorded as found				
"	51 "	100	"	"	"	to the nearest 5
"	101 "	250	"	"	"	" " "
"	251 "	500	"	"	"	" " "
"	501 "	1,000	"	"	"	" " "
"	1,001 "	10,000	"	"	"	" " "
"	10,001 "	50,000	"	"	"	" " "
"	50,001 "	100,000	"	"	"	" " "
"	100,001 "	500,000	"	"	"	" " "
"	500,001 "	1,000,000	"	"	"	" " "
"	1,000,001 "	10,000,000	"	"	"	" " "

The counting stand is usually marked to facilitate counting, for example, by concentric circles and lines through the center forming sectors. With high numbers four opposite sectors may be counted, situated at right angles to each other, and multiplied by a factor.



Examination for *B. coli*

*B. coli* (bacillus of the colon) represents a group of bacteria inhabiting the large intestines of man and animals. Its presence in water supply signifies possible sewage contamination and the latter means probable typhoid, dysentery, etc., germs. In fact if a drinking water becomes contaminated by sewage an increase in typhoid fever is almost certain to follow. Animals do not spread typhoid though they may be a factor in paratyphoid. *B. coli* in a water supply may be due to harmless sources and so of little significance.

The following new sub-classification is recommended in "Standard Methods of Water Analysis," 1920, A. P. H. A.:

<i>B. coli</i> of fecal origin .....	Methyl red + Voges-Proskauer - Gelatin - Adonite - Indol, usually + Saccharose, usually - Methyl red - Voges-Proskauer +
<i>B. aërogenes</i> of fecal origin .....	Gelatin - Adonite + Indol, usually - Saccharose + Methyl red - Voges-Proskauer +
<i>B. aërogenes</i> , probably not of fecal origin .....	Gelatin - Adonite - Indol, usually - Saccharose + Methyl red - Voges-Proskauer +
<i>B. cloacae</i> may or may not be of fecal origin .....	Gelatin + Adonite + Indol, usually - Saccharose +

Procedure for the above identifications may be found in "Standard Methods of Water Analysis," 1920 edition, published by American Public Health Association.

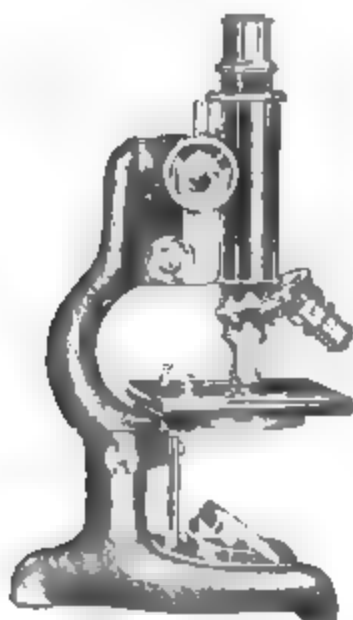


FIG. 176. Microscope for Bacteriological Examination.

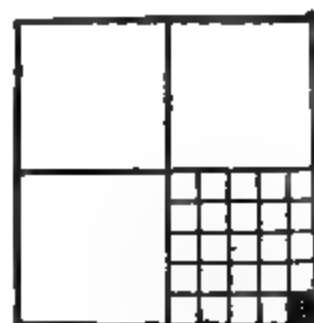


FIG. 177. Ocular Micrometer.

Subclassification of *B. coli*<sup>1</sup>

***B. coli* Group.** The general characteristics common to this group are:

Fermentation of dextrose and lactose with gas formation, short bacillus with rounded ends, non-spore-forming, facultative anaërobe, gives positive test with esculin, grows at 20° C. on gelatine and at 37° C. on agar, non-liquefying in fourteen days on gelatine, gram-staining negative.

The group consists of four species:

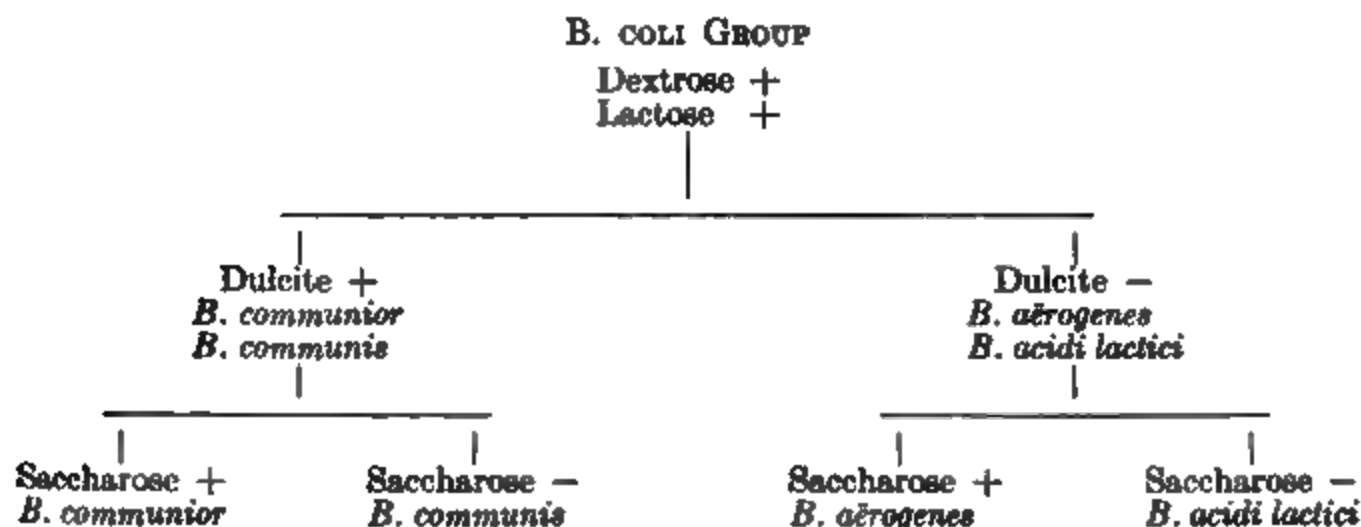
*B. communior* (Durham).

*B. communis* (Escherich).

*B. aërogenes* (Escherich).

*B. acidilactici* (Hüeppe).

This group is differentiated as follows:



The revised "Standard Methods" in testing for the *B. coli* group require gas formation in lactose broth plus confirmation in accordance with the following procedure:

<sup>1</sup> Adopted by A. P. H. A., 1912, and recommended by the author.

# 1464 BACTERIOLOGICAL EXAMINATION OF WATER

## Summary of Steps Involved in Making Presumptive, Partially Confirmed and Completed Tests for *B. Coli*

Steps in Procedure	Further Procedure Required
I. Inoculate lactose broth fermentation tubes; incubate 24 hrs. at 37° C.; observe gas-formation in each tube.	
1. Gas-formation, 10 per cent or more; constitutes positive presumptive test.	
(a) For other than smallest portion of any sample showing gas at this time, and for all portions, including smallest, of sewage and raw water this test is sufficient.....	None
(b) For smallest gas-forming portion, except in examinations of sewage and raw water.....	III
2. Gas-formation less than 10 per cent in 24 hrs.; inconclusive.....	II
II. Incubate an additional 24 hours, making a total of 48 hours incubation; observe gas-formation.	
1. Gas-formation, any amount; constitutes doubtful test, which must always be carried further.....	III
2. No gas-formation in 48 hours; constitutes final negative test.....	None
III. Make plate* from smallest gas-forming portion of sample under examination; incubate 18 to 24 hours; observe colonies.	
1. One or more colonies typical in appearance.	
(a) If only "partially confirmed" test is required.....	None
(b) If completed test is required, select two typical colonies for identification.....	V
2. No typical colonies.....	IV
IV. Replace plate in incubator for an additional 18 to 24 hours; then, whether colonies appear typical or not, select at least two of those which most nearly resemble <i>B. coli</i> .....	V
V. Transfer each colony fished to:	
1. Lactose broth fermentation tube; incubate not more than 48 hrs. at 37° C. Observe gas-formation.....	None
2. Agar slant; incubate 48 hours at 37° C.	
(a) If gas formed in lactose broth tube inoculated with corresponding culture.....	VI
(b) If no gas formed in corresponding lactose broth tube, test is completed and negative.....	None
VI. Make stained cover-slip or slide preparation, and examine microscopically.	
1. If preparation shows non-spore-forming bacilli in apparently pure culture, demonstration of <i>B. coli</i> is completed.....	None
2. If preparation fails to show non-spore-forming bacilli or shows them mixed with spore-bearing forms or bacteria of other morphology.	VII
VII. Replate, to obtain assuredly pure culture, select several colonies of bacilli and repeat steps V and VI.	

\* Endo- or Lactose-litmus-agar.

## BACTERIOLOGICAL EXAMINATION OF WATER 1465

"Standard Methods" outlines the following procedure arranged by days:

### Routine Procedure for Examination of Samples of Water

#### First Day:

1. Prepare dilutions as required.
2. Make two (2) gelatin plates from each dilution, and incubate at 20° C.
3. Make two (2) agar plates from each dilution, and incubate at 37° C.
4. Inoculate lactose broth fermentation tubes with appropriate amounts for *B. coli* tests, inoculating two (2) tubes with each amount.

**NOTE.** Where repeated tests are made of water from the same source, as is customary in the control of public supplies, it is not necessary to make duplicate plates or fermentation tubes in each dilution. It is sufficient, in such circumstances, to make duplicate plates only from the dilution which will most probably give from 25 to 250 colonies per plate.

#### Second Day:

1. Count the agar plates made on the first day.
2. Record the number of lactose broth fermentation tubes which show 10 per cent or more of gas.

**NOTE.** In case only the presumptive test for *B. coli* is required, fermentation tubes showing more than 10 per cent of gas at this time may be discarded.

#### Third Day:

1. Count gelatin plates made on first day.
2. Record the number of additional fermentation tubes which show 10 per cent or more of gas.
3. Make a lactose-litmus-agar or Endo's medium plate from the smallest portion of each sample showing gas. Incubate plate at 37° C.

**NOTE.** In case the smallest portion in which gas had been formed shows less than 10 per cent of gas, it is well to make a plate also from the next larger portion, so that, in case the smallest portion gives a negative end result it may still be possible to demonstrate *B. coli* in the next larger dilution.

#### Fourth Day:

1. Examine Endo's medium or lactose-litmus-agar plates. If typical colonies have developed, select two and transfer each to a lactose broth fermentation tube and an agar slant, both of which are to be incubated at 37° C.
2. If no typical *B. coli* colonies are found, incubate the plates another 24 hours.

#### Fifth Day:

1. Select at least two colonies, whether typical or not, from the Endo's medium or lactose-litmus-agar plates which have been incubated an additional 24 hours; transfer each to a lactose broth fermentation tube and an agar slant, and complete the test as for typical colonies.
2. Examine lactose broth fermentation tubes inoculated from plates on the previous day. Tubes in which gas has been formed may be discarded after the result has been recorded. Those in which no gas has formed should be incubated an additional 24 hours.

**Sixth Day:**

1. Examine lactose broth fermentation tubes reincubated the previous day.
2. Examine microscopically agar slants corresponding to lactose fermentation tubes inoculated from plate colonies and showing gas-formation.

The above procedure is too troublesome for a laboratory handling large numbers of routine samples. The work is too great and the time too long for the value of the results. It was adopted because of the fact that *B. welchii*, a spore-forming group (though probably of fecal origin), also forms gas in lactose media. *B. welchii* is obligate anaerobic. Gram positive, esculin negative, and a spore-former. It may easily be differentiated from *B. coli* by its appearance in a hanging drop. (Prepare hanging drop by placing a drop of salt solution, 0.85% sodium chloride, on a sterile coverglass and mix with a minute portion of the culture, taken direct from the fermentation tube. Invert this cover slip over a hollow slide, sealed by a ring of vaseline, and examine under the microscope.) It is a large, non-motile bacillus, occurring in chains particularly when grown in lactose bile media, as mentioned in the 1912 edition of "Standard Methods." Recently in a few instances aerobic spore-forming bacilli have been described which fermented lactose broth, but such instances are extremely rare.

Since about one-third of the laboratories of the country are still using bile media it seems fitting to include in this chapter a new modification, "Brilliant-green lactose peptone bile" (see Preparation of Media) which eliminates *B. welchii* from the test. This modification, worked out by Muer & Harris, bacteriologists at Mt. Prospect Laboratory, Brooklyn, has been in use for over a year in the New York City Water Department Laboratories with entire satisfaction. It makes the presumptive test for *B. coli* a practical certainty. Attention should be called to the fact, and emphasized, that since the 1912 standards were published lactose bile has been made more delicate by the use of only 5% bile and also in considering 10% or more of gas a positive test. Now the introduction of "brilliant-green" eliminates the *B. welchii* group. Confirmation of *B. coli* has never failed in all cases tried. The only reason for making 10% of gas a lower limit is because of possible danger of inversion of a small amount of lactose to dextrose during sterilization. It is however very rarely that there is less than 10% of gas.

In testing for *B. coli* 0.1 cc., 1 cc., and 10 cc. portions of water are introduced to the bottom of the bile tubes, or in polluted waters quantities varying by decimal multiples or fractions until a negative test is obtained. Sewage will usually show a positive test in 0.000001 cc. The plantings are made at the same time that the plates are prepared for total counts. The tubes are incubated at 37° C. for three days. Ten per cent of gas within three days is a positive test.

**Examination for *B. Typhi*, etc.**

Direct test for *B. typhi* may be made from the bile tube or from larger quantities of water incubated in bottles of bile. The method of the 1912 edition of "Standard Methods" is still in use in the New York City Water Laboratories as a routine procedure. Dilutions from the bile tube media are mixed with 10 cc. melted Hesse agar (see Preparation of Media) in petri dishes with porous tops. The poured plates are hardened in the ice-box and then incubated 24 hours at 37° C. The colony is characteristic only when a few colonies are on a plate. They are large size, have a dense white nucleus, then translucent zone, then dense white seam. The colonies are perfectly round. They retain their appearance if placed in the ice-box, and as they develop further produce another translucent area and another seam, etc., giving the appearance of concentric rings. Other large colonies of other species usually become dense throughout. Forms most likely to interfere are *B. paratyphi*, *B. pyocyaneus*, *B. fluorescens liquefaciens*, and some very motile forms of *B. coli*.

From the edges of the colony direct tests should be made for *B. typhi* and *B. paratyphi* by specific agglutination tests.

**Widal Test.** To make the Widal test place a small portion of the culture in a drop of normal salt solution on a cover glass, and invert it over a rubber ring on a glass slide, using vaseline on the edges so as to prevent evaporation and consequent movement by currents in the drop.

If the bacteria are motile rods resembling *B. typhi* add a drop of equal size of highly diluted anti-typhoid serum (the latter diluted with physiological salt solution). If in the course of half an hour the bacteria cease their motions and agglutinate, the presence of *B. typhi* is practically established. In rare cases, some strains of *B. coli* and allied species may respond to the Widal test, but almost invariably in dilutions of 1-50 or less. The high-power dry lens is best for this work.

To determine the point of highest dilution at which agglutination takes place the Widal test is best made in tubes and examined macroscopically. Place a series of small test tubes in a rack and pour into each varying dilutions of anti-typhoid serum. To each tube add an equal amount of 24-hour broth culture of *B. typhi* and incubate at 37° C. for at least three hours. The highest point at which precipitation takes place is the highest point of agglutination.

**Russell Media.** As additional rapid means of differentiating between *B. typhi* and *B. para-typhi* A and B, needle stabs may be made into tubes of Russell media (see Preparation of Media) and incubated at 37° C. The reactions are based on the fact that the bacilli growing aerobically, that is on the slant, only utilize the carbohydrate when present in amounts over 0.1%, whereas, growing anaerobically stabbed in the butt, they must utilize the carbohydrates for their oxygen supply and therefore ferment the trace of glucose present. The indications of the Russell media reactions are as follows:

<i>B. coli</i> Group—Russell media—		Slant, acid	(Glucose, acid and gas)
		Butt, acid and gas	(Lactose, acid and gas)
<i>B. typhi</i> Group	} Russell media	Slant unchanged	(Glucose, acid only)
<i>B. dysentery</i> Group		Butt, acid only	(Lactose, not fermented)
<i>B. paratyphi</i> Group	} Russell media	Slant unchanged	(Glucose, acid and gas)
<i>B. enteritidis</i> Group		Butt, acid and gas	(Lactose, not fermented)
<i>B. alkaligenes</i> Group—Russell media—		Slant unchanged	(Glucose, not fermented)
		Butt unchanged	(Lactose, not fermented)

In distinguishing between typhoid and dysentery (true or Shiga type)—typhoid bacilli are motile, dysentery non-motile, typhoid produces acid in mannite, dysentery does not.

There also exist three types of para-dysentery (non-motile): Type I (Park-Hiss), type II (Flexner) and type III (Strong). Para-dysentery are different from true dysentery in that they produce acid with mannite (the same as typhoid) but they all give positive indol, while dysentery and typhoid do not. Indol is sometimes doubtful with Flexner. The three para-dysentery groups are further distinguished among themselves by their reactions upon maltose and saccharose. The type I produces acid in neither, type II produces acid in maltose but not in saccharose, type III produces acid in saccharose but not in maltose. The usual final test for all these different types of typhoid and dysentery is the agglutination with specific serums. The sugar fermentation tests must be made upon freshly isolated cultures since after artificial cultivation Park-Hiss strains may ferment maltose and Flexner strains saccharose as demonstrated by Hiss and by Lentz.

The members of the typhoid, para-typhoid, dysentery and para-dysentery groups all form colorless colonies upon Endo media. This is frequently the starting point for isolation.

#### REFERENCES

- "Standard Methods of Water Analysis." Am. Pub. Health Assoc., Editions 1905, 1912, 1917 and 1920. (Contain extensive bibliography.)  
 Park and Williams, "Pathogenic Microorganisms."  
 Prescott and Winslow, "Elements of Water Bacteriology."  
 Chester, "A Manual of Determinative Bacteriology."

# METHODS FOR THE DETERMINATION OF SOLUBILITY\*

ATHERTON SEIDELL<sup>1</sup>

A quantitative determination of a solubility consists essentially of two operations; the preparation of the saturated solution and its subsequent analysis. In those cases where these steps are performed separately the method may, in general, be designated as the analytical and in those where they are combined, as the synthetic. In both cases, however, the consideration of first importance is the assurance that final equilibrium between solvent and solute has been reached. Since this point is that at which no further change occurs in the relation between the amount of the compound in solution and that remaining undissolved, the only criterion of saturation is the evidence that the concentration of the solution has not changed during a longer or shorter interval of time, during which those conditions which would tend to promote such a change have been allowed to operate.

Of the conditions which promote most effectively the attainment of equilibrium between a solute and a solvent, the provision for the intimate contact of the two is most important. In other words, only by the thorough mixing which agitation or effective stirring provides can the point of saturation be reached with certainty. In the case of the reciprocal solubility of liquids, the point of equilibrium is usually attained within a much shorter period than in the case of solids dissolved in liquids. In the latter case, the necessary disintegration of the solid, incident to its solution in the liquid, is a process which is restricted to the surface layers of the solid, and, therefore, unless a large area, such as a finely divided state provides, is available, and unless that portion of the solvent which has acted upon a given surface area is repeatedly replaced by fresh solvent, the process of solution will be greatly retarded. It is quite evident that, although a solution in contact with even very finely divided solid may promptly become saturated in the immediate vicinity of the solid without stirring, the distribution of the dissolved material to the remainder of the solvent would depend upon diffusion, and since the rate at which this proceeds would diminish as the concentration differences became equalized, the process would take place at a gradually diminishing rate. If the point of equilibrium is approached from supersaturation, the above remarks apply with equal effect, since only at the surface of the solid can the excess of salt leave the solution and, without other provision than diffusion for successively bringing the entire amount of the solution in contact with the solid, the deposition of the excess of dissolved material can occur only at a very slow rate. The importance of active and continuous agitation of the solid and solution, in effecting saturation, cannot, therefore, be too strongly emphasized. It may in fact be assumed that determinations of the solubility of solids, made without continuous agitation, are always open to the suspicion that the results do not represent the final equilibrium which such data are required to show.

\* Reprinted from 2nd. Ed. of "Solubilities."

<sup>1</sup> Hygienic Laboratory, U. S. Public Health Service, Washington, D. C.



Since solubility is a function of temperature, the accurate control of the temperature in making a solubility determination is another one of the indispensable requisites of accuracy. In general, it may be stated therefore, that every procedure designed for preparing a saturated solution must include provision for the accurate control of the temperature and for active and continuous agitation or stirring of the solution. In the case of the solubility of gases, which will be considered in a separate section, provision for the control of the pressure must also be made.

It is obvious that since the solubilities of various compounds differ, and that of one compound is affected by the presence of another, the accurate determination of this constant for a particular molecular species presupposes that only this one substance is present in the pure solvent. That is, accuracy of results demand that only pure compounds be involved in a given determination, consequently, no effort should be spared to make it certain that the highest possible purity of both solute and solvent has been attained.

*Apparatus for the Determination of the Solubility of Solids by the Analytical Method.* The types of apparatus which have been developed for the preparation of saturated solutions of solids in liquids differ principally in respect to whether designed for multiple or single determinations at a given temperature. Examples of the first type are illustrated by Figs. 178 and 179.

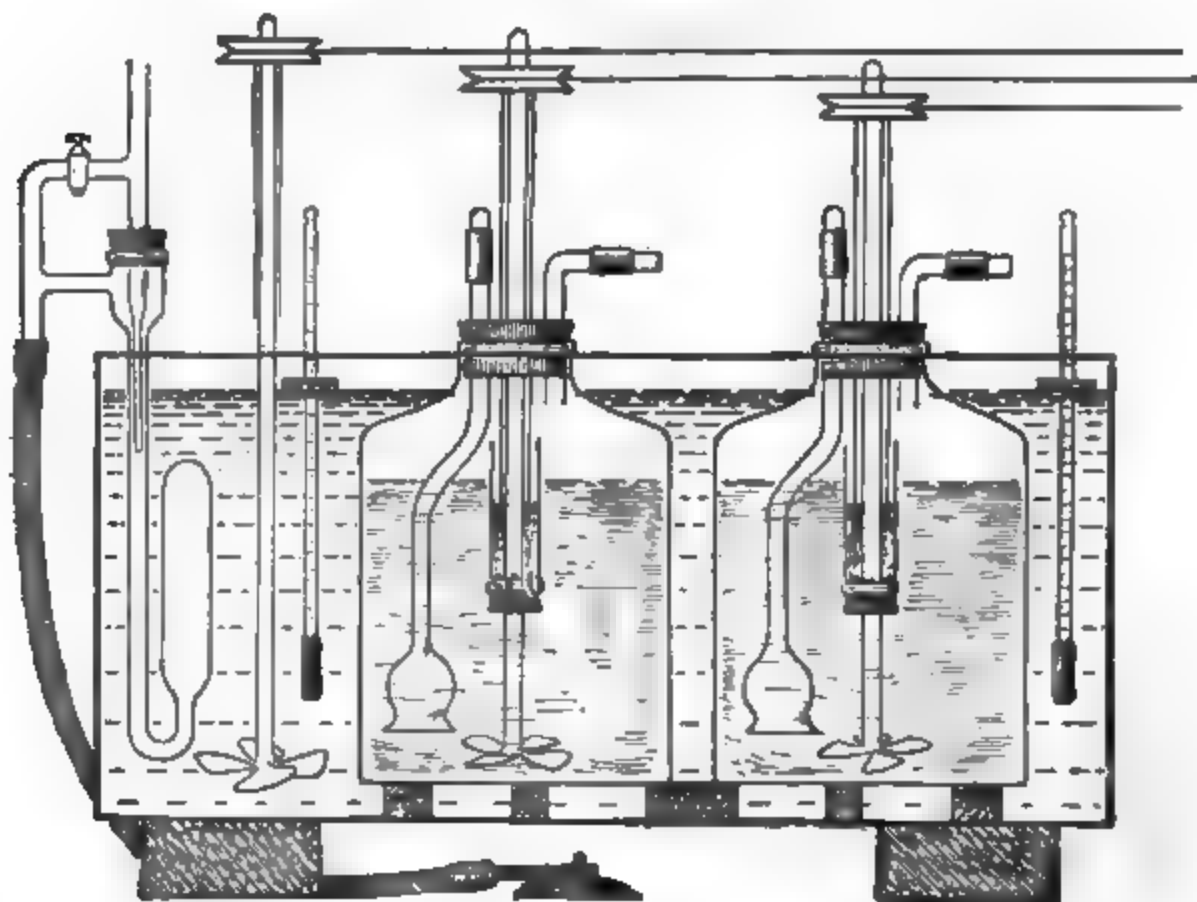


FIG. 178. Determination of Solubility of Solids.

It will be noted that in one case (Fig. 178) the bottles containing the solutions are stationary and the liquid in each and in the constant temperature bath is kept in motion by means of revolving stirrers. This form of apparatus was used by Moody and Leyson (1908) for the determination of the solubility

of lime in water and is particularly adapted for relatively slightly soluble compounds for which rather large quantities of the saturated solution are needed for accurate analysis. There is also shown in the figure the provision for withdrawing the saturated solution through a filter within the inverted thistle tube. The stirrers in the bottles are fitted with mercury seals to prevent access of air containing carbon dioxide. Other features of the apparatus will be readily understood from the drawing.

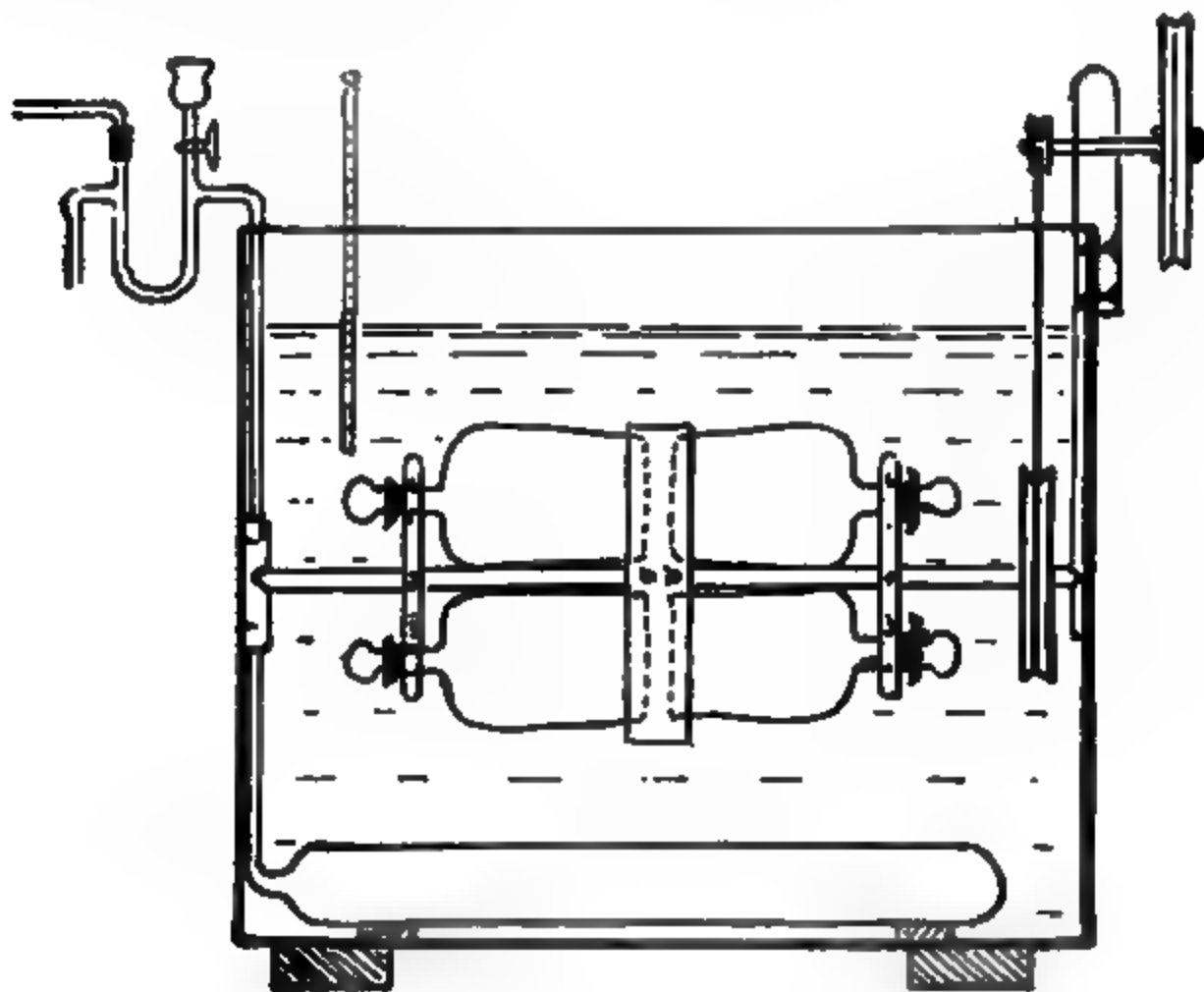


FIG. 179. Noyes apparatus for determining the solubility of solids.

A more common type of apparatus, designed for the simultaneous saturation of several solutions at the same temperature, is that illustrated by Fig. 179, in which the bottles containing the solutions are slowly rotated in the constant temperature bath. The form shown is that described by Noyes (1892). This type of apparatus has the advantage that the solid is, to a large extent, kept in suspension in the liquid and, therefore, offers the most favorable opportunity for continuous and uniform contact with the solution. Many examples of this form of apparatus, differing principally in size and in the direction of movement of the containers, are described in the literature.

Of the second type of apparatus, designed for a single determination at a given temperature, many varieties have been developed for particular conditions. Of these, the following examples have been selected as typical of this class and, it is hoped, will illustrate most of their desirable features. They are, in general, adaptations of earlier designs and it is not intended that the

name given in connection with each is that of the investigator who deserves the credit for originating the type. The drawings will, for the most part, be readily understood without detailed explanations. The dimensions are not stated, since they can usually be varied to suit the needs of almost any problem.

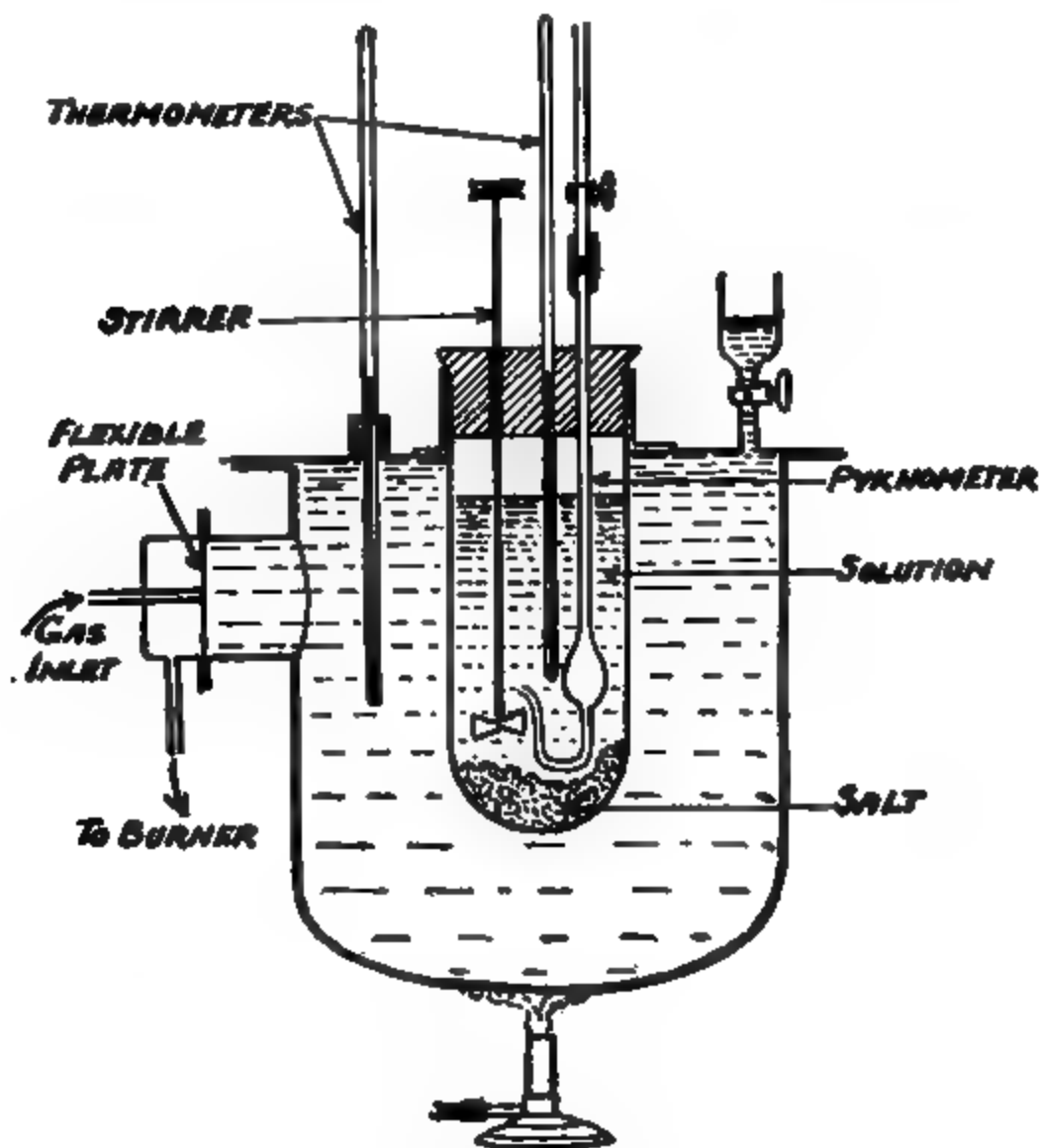


FIG. 180. Berkeley's apparatus for determining solubility.

In Fig. 180 is shown the apparatus used by the Earl of Berkeley (1904) for the very careful determinations of the solubility of inorganic salts in water. The features of particular interest in connection with it are, that the water bath itself is made to serve as the temperature regulating device, and the apparatus for withdrawing and simultaneously filtering the saturated solution is a combination of pipet and pycnometer. This was provided with ground glass caps for each end and the stem was accurately graduated. It was, of course, carefully standardized before use. The flexible iron plate shown was made of a disc from the receiver of a telephone. The apparatus was used for determinations at temperatures between  $30^{\circ}$  and  $90^{\circ}$  and the range of variations from the set temperature of the bath was, for 2-3 hour periods, within about  $0.2^{\circ}$ . For the inner vessel containing the salt, the range was about  $0.05^{\circ}$ . At each temperature two determinations of density and solubility were made; one on the solution obtained by stirring a supersaturated solution in

contact with solid salt, and the other on the solution obtained by stirring an unsaturated solution in contact with an excess of salt.

In the case of determinations at the boiling point a special apparatus was required. Two forms, described by the Earl of Berkeley (1904), are shown in Figs. 181 and 182. The first was used for the less soluble salts and consisted of an

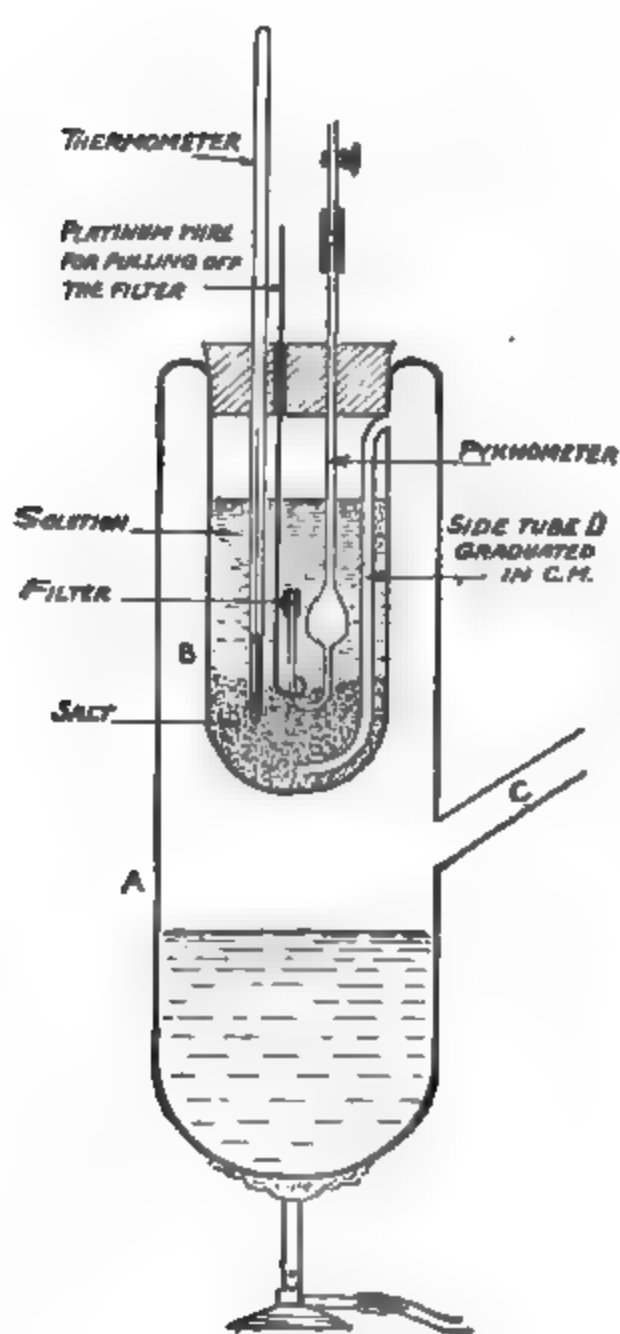


FIG. 181.

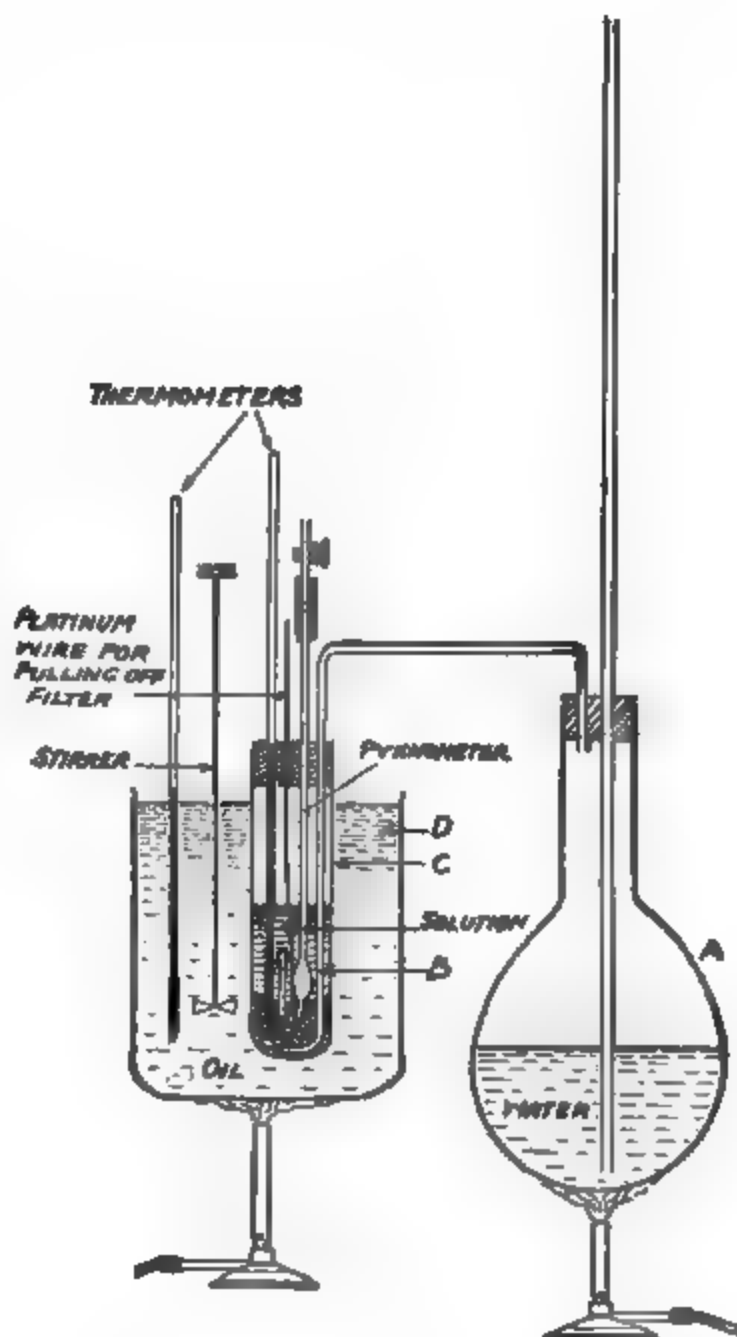


FIG. 182.

Berkeley's apparatus for determining solubility.

outer tube *A* containing water and an inner tube *B* containing salt and solution. By boiling the water vigorously and closing the side tube *C*, steam passing through the tube *D* stirred the solution thoroughly and the temperature rose to the boiling point of the saturated solution and remained constant when saturation was attained. The second form of apparatus (Fig. 182) was devised for use with extremely soluble salts. In these cases it was found that the larger quantity of steam required for thorough stirring dissolved so much salt

that it was necessary to have a very large excess present. In this apparatus the steam was generated in a boiler *A* and conducted through the tube *B* to the bottom of the large test tube *C* containing the excess of salt and solution. The test tube was immersed in the oil bath *D* which was vigorously stirred and maintained at a temperature close to that of the boiling point of the saturated

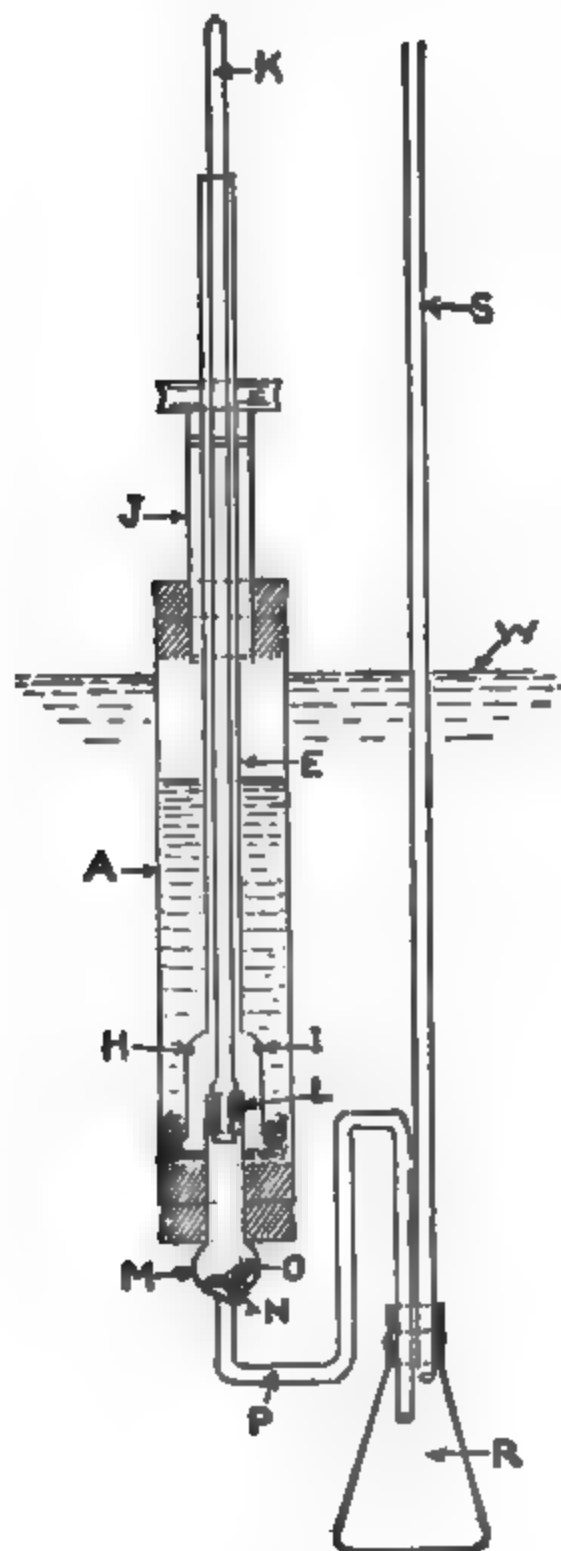


FIG. 183.

Victor Meyer type of apparatus for solubility determination.

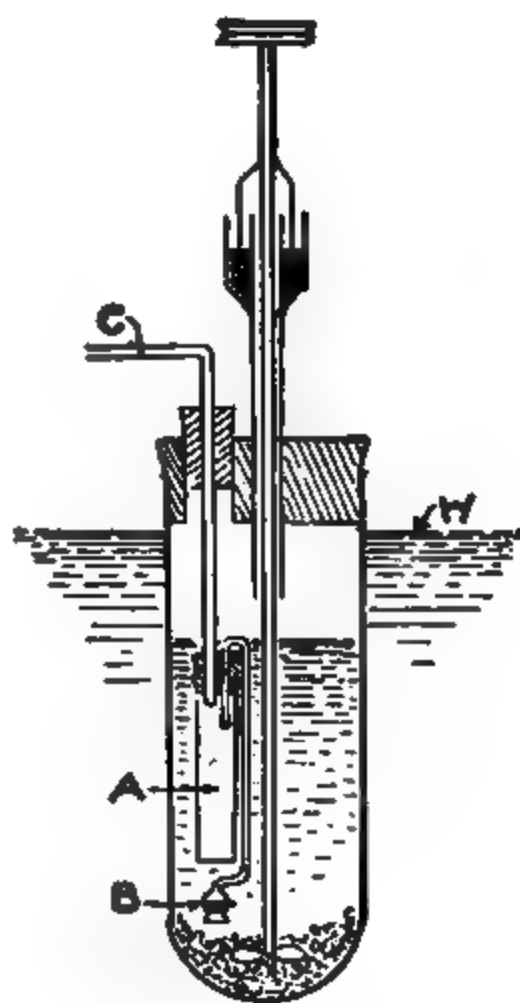


FIG. 184.

Walton and Judd apparatus for solubilities.

solution. When the temperature of the oil bath was below the boiling point salt dissolved; when above, salt was thrown out of solution. Considerable difficulty was experienced in filling the pycnometer with the saturated solution without introducing errors due to steam bubbles caused by the suction which was applied.

A comparatively simple form of the type of apparatus used by Victor Meyer in 1875 and modified by Reicher and van Deventer (1890) and by Goldschmidt (1895), is described by Hicks (1915) and shown in the accompanying Fig. 183. A glass cylinder *A* is closed at each end with large one-hole rubber stoppers. The mixture of salt and solution is contained in this cylinder and is stirred by the rotation of the tube *E* which is provided with an enlargement at its lower end in which there are two small holes at *H* and *I*. The stirrer rotates in the bearing formed by the hollow wooden cylinder *J*. The glass rod *K* carries a rubber stopper *L* which closes the filtering tube *M*, in which a platinum cone *N* supports an asbestos filter *O*. The siphon *P* connects the filtering tube with the flask *R* which is provided with an outlet through the small tube *S*. The apparatus is immersed in a constant temperature water bath *W*, to about the level shown. After stirring the mixture of salt and solution a sufficient length of time for attainment of saturation, the undissolved salt is allowed to settle and the rubber stopper is withdrawn from the filter tube by means of the glass rod *K*. Suction is applied through the tube *S* to hasten the filtering and the clear solution collected, at the temperature of the bath, in the previously weighed flask *R*.

A similar apparatus was used by Walton and Judd (1911), for determination of the solubility of lead nitrate in pyridine. This is shown in Fig. 184 and consists of a glass test tube fitted with a stirrer which turns in a mercury seal, thus preventing loss of solvent by evaporation or the admission of moisture from the air. To take a sample of the saturated solution, the weighing tube *A* was introduced into the larger tube through a hole in the stopper. After reaching the temperature of the bath the stirrer was stopped, the end of the small tube *B*, which was covered with a piece of closely-woven muslin, was dipped below the surface of the solution and the liquid drawn into *A* by applying suction at *C*. The tube *A* was then removed, weighed and the contents analyzed.

An apparatus which was used by Donnan and White (1911), for the determination of equilibrium in the system palmitic acid and sodium palmitate is shown in Fig. 185. The stirring in this case was accomplished by means of a

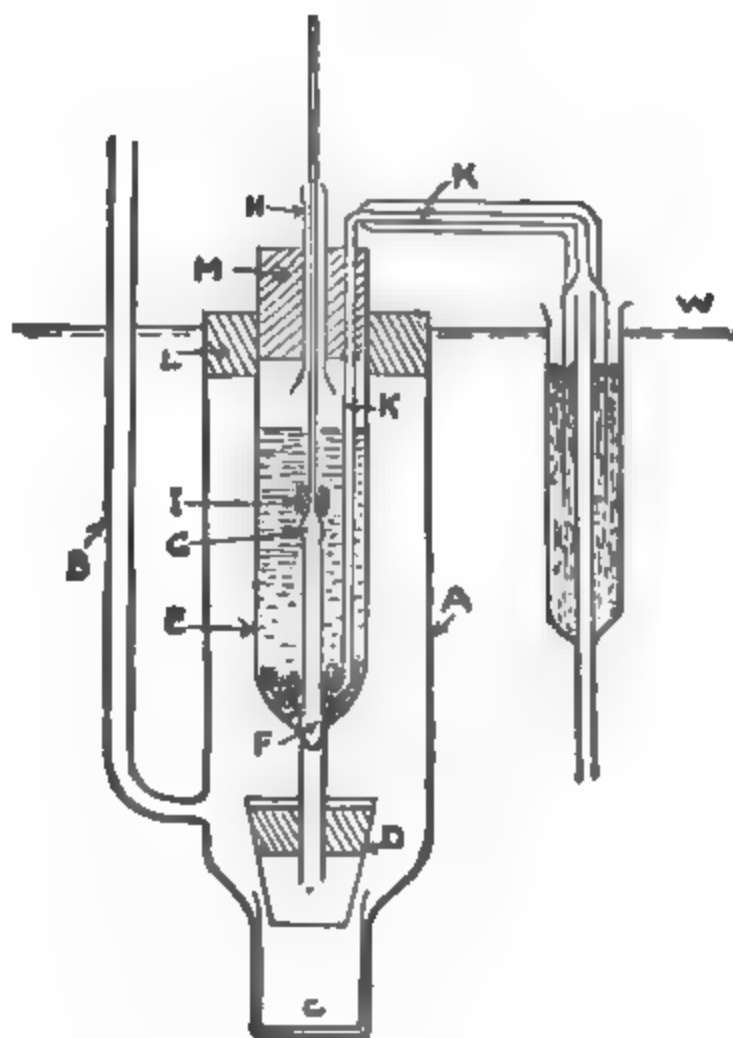


FIG. 185. Donnan and White apparatus for determining solubilities.

current of dry air, free of carbon dioxide. The apparatus consists of two parts, namely, an inner chamber *E*, where equilibrium was attained, and an outer case *A*, designed for isothermal filtration. The whole was immersed in a thermostat to the level *W*. A side tube *B* permitted connection with a filter pump. *C* is a weighing bottle to receive the filtered saturated solution and *D* a Gooch crucible provided with a paper filter. The cork, closing *A*, was covered with a plastic layer to render it airtight. The tube at the lower end of *E* was closed with a ground glass plug *F*, the stem of which was enlarged to a small bulb at *G* and then drawn out to pass easily through *H*, leaving an air

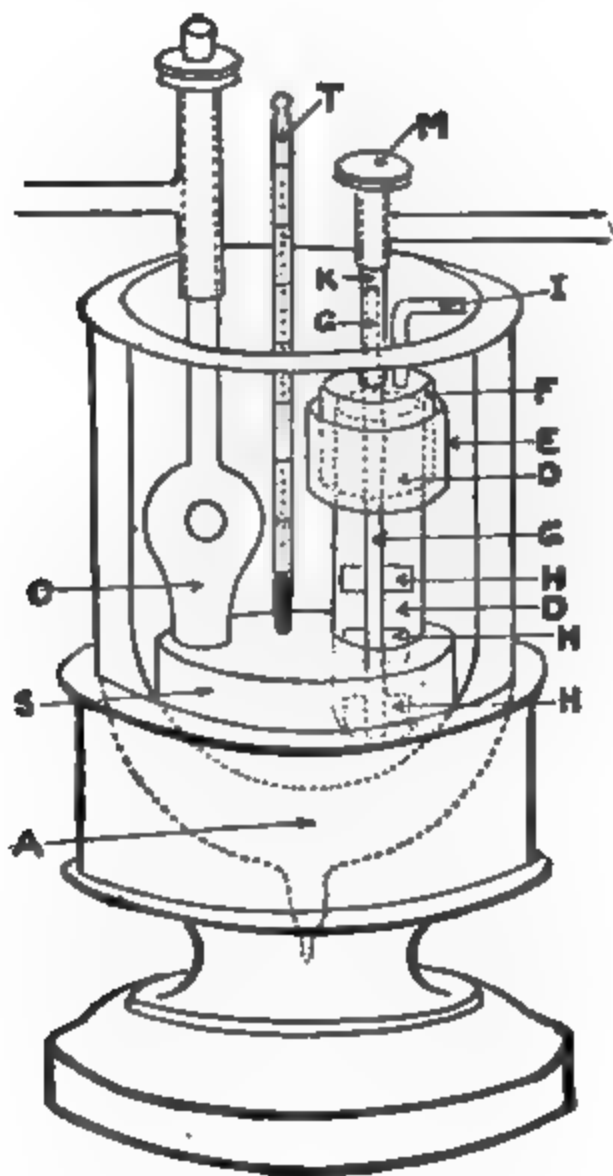


FIG. 186. Cohen and Inouye apparatus for solubilities.

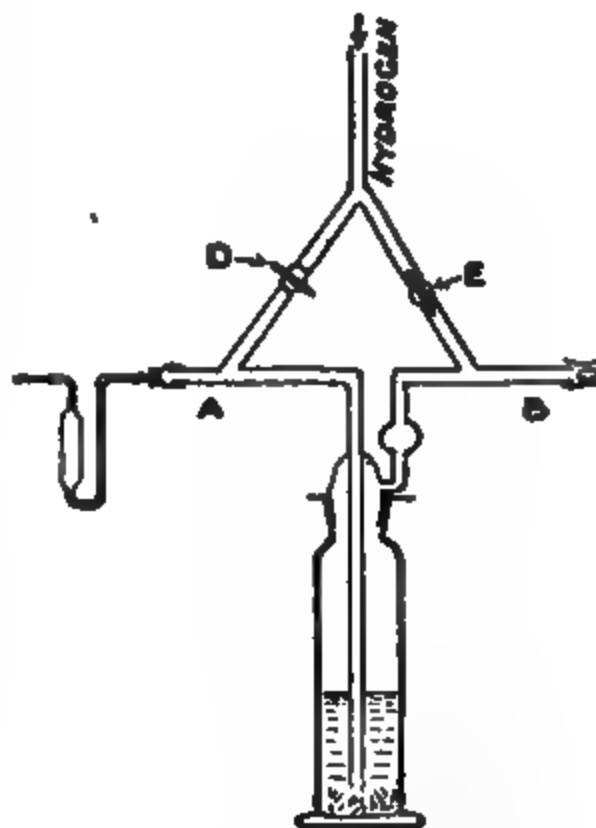


FIG. 187. Bahr's apparatus for determining solubilities.

free outlet around it. The small cork *I* was used to support the stopper when lifted to allow the contents of *E* to flow down for filtration. The dry air by which the mixture was stirred was drawn through *K* by applying suction at *H*. The preheating of this air was accomplished by drawing it through a thin spiral immersed in the thermostat. The connection between the equilibrium apparatus and preheater was made through a mercury seal, which permitted lifting the apparatus easily without damage to the fragile preheater permanently mounted in the bath. This apparatus provided for the recovery, separately, of

the saturated solution and undissolved solid. These authors also describe an improved electrically heated and controlled constant temperature bath.

Determinations at lower temperatures that can be constantly maintained with the aid of a water bath require special forms of apparatus which permit of temperature control under more or less restricted conditions. An apparatus of this type, which was used by Cohen and Inouye (1910), for determination of the solubility of phosphorus in carbon disulfide, is shown in Fig. 186, and is intended for the range of temperature between  $-10^{\circ}$  and  $+10^{\circ}$ . The saturating vessel *D* consists of a glass cylinder to the upper end of which is cemented a steel collar *E*, containing a deep channel. A mixture of litharge and glycerol was used as the cementing material for this purpose. The inverted steel cover *F* fits into the channel of this collar and the seal of the joint is effected, in the usual way, by means of a layer of mercury. The cover *F* is provided with a brass tube *K*, to which the pulley *M* is attached, and is also pierced by the tightly cemented-in glass tube *I*. The glass rod *G*, containing on its lower end the three stirring wings *H H H*, is cemented into the brass tube *K*. The saturating vessel is, for stability, tightly fastened in a hole in a block of lead, *S*, contained in the Dewar cylinder *A*. An atmosphere of  $\text{CO}_2$  in the saturating vessel is provided by introducing  $\text{CO}_2$  under pressure through *I* and allowing the excess to escape through the mercury seal in *E*. After charging the apparatus, *I* is closed with a rubber tube and plug and the stirrers *H H H* set in motion. A Witt stirrer, *O*, keeps the contents of the bath in rapid circulation. Water is used in the bath for temperatures above  $0^{\circ}$ , and alcohol for those below  $0^{\circ}$ . The regulation of the temperature is accomplished by addition of ice or solid  $\text{CO}_2$  as found necessary and, therefore, requires very close attention on the part of the experimenter.

A novel and simple form of apparatus, which was used by Bahr (1911), for the determination of the solubility of thallium hydroxide at temperatures up to  $40^{\circ}$  is shown in Fig. 187. As will be seen, this consists of a gas washing flask to the arms of which a *Y* tube provided with two stop-cocks is sealed. The inside walls of the apparatus were coated with hard paraffin and the required amounts of thallium hydroxide and water introduced. It was then immersed in a water bath and the contents stirred by means of a current of hydrogen, which entered as shown and with *A* and *E* closed, passed through *D* and out at *B*. When it was desired to remove a sample of the solution for analysis, *B* and *D* were closed and the liquid forced through *A* into the pycnometer by means of gas pressure entering through *E*. For temperatures above  $40^{\circ}$ , the form of apparatus shown in Fig. 188 was used. In this case *K* represents a copper cylinder with double walls, of which the inner compartment *G*, contains concentrated salt solution which is stirred by a stream of air (not shown), and the outer compartment contains a layer of heating liquid *H*. The glass tube *L* contains the mixture of thallium hydroxide and water which is stirred by means of a current of hydrogen (not shown). When saturation is attained the tube *A*, of small bore and thick walls and provided with a small



asbestos filter, is introduced and the saturated solution forced over into the receptacle *B* by pressure of hydrogen which enters at *C*. The heating liquid in *B* is the same as used in *H*. The following heating liquids with the boiling points shown were used: Allyl chloride, 46°; Ethylene chloride, 55°; Chloroform, 61°; Methyl alcohol, 66°; Benzene, 80°; Benzene-Toluene mixture, 91°; Water, 100°.

A somewhat more elaborate apparatus, in which the constant temperature is maintained by means of the vapor of a boiling liquid, is shown in Fig. 189.

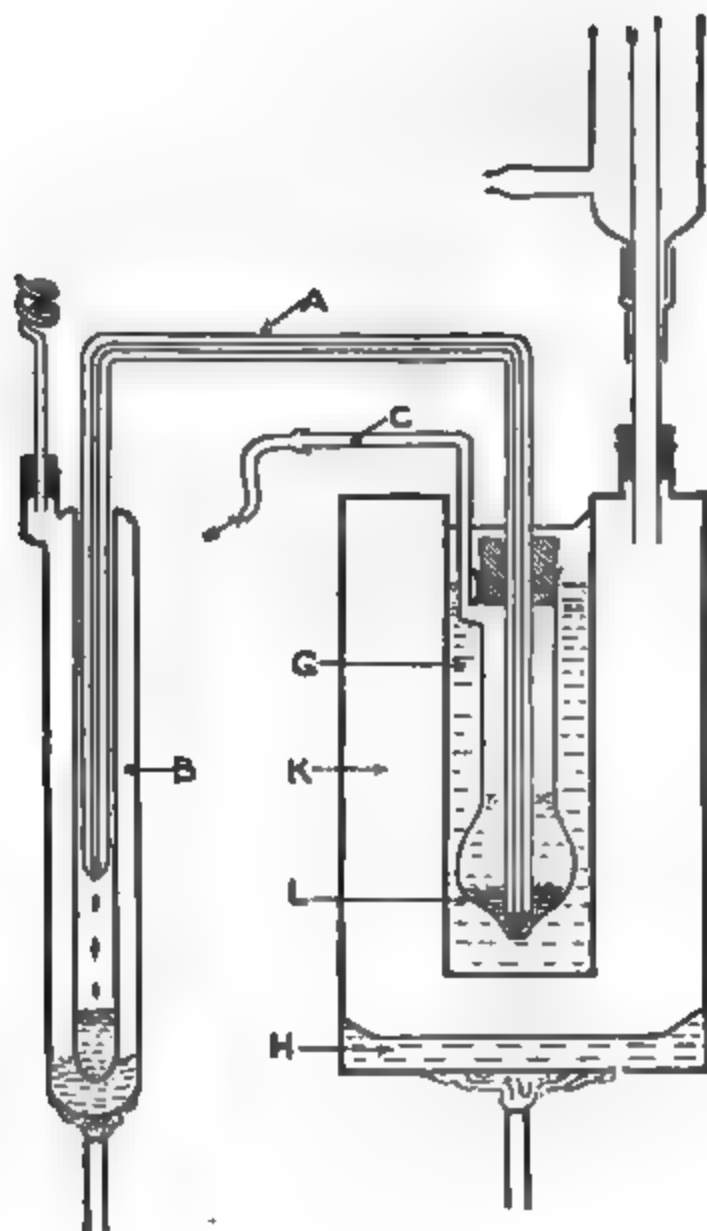


FIG. 188.

This apparatus was developed by Tyrer (1910) for the very accurate determination of the solubilities of anthraquinone, anthracene and phenanthraquinone in single and mixed organic solvents. The solvent with excess of the solute was placed in *A* and kept in constant agitation by means of the vertically acting stirrer shown. The tube *A* is surrounded by a bath of vapor which circulates through the cylinder *B*, condenses in *C*, and returns to the boiling flask *M*. When the solution is saturated it is allowed to settle, and the clear solution run out (by raising the tube *D*) into a small graduated flask *E*, which is maintained at the same temperature as the solution *A*. The temperature of the vapor bath is varied by changing the pressure under which the liquid in

the flask *M* is boiling. For this purpose, the manostat *P* is provided. The temperature can, with care, be maintained constant to  $0.01^{\circ}$ . For this purpose the apparatus must be airtight, the liquid in the boiling flask must not bump (which is entirely prevented by placing a layer of mercury in the flask) and a pure boiling liquid must be used.

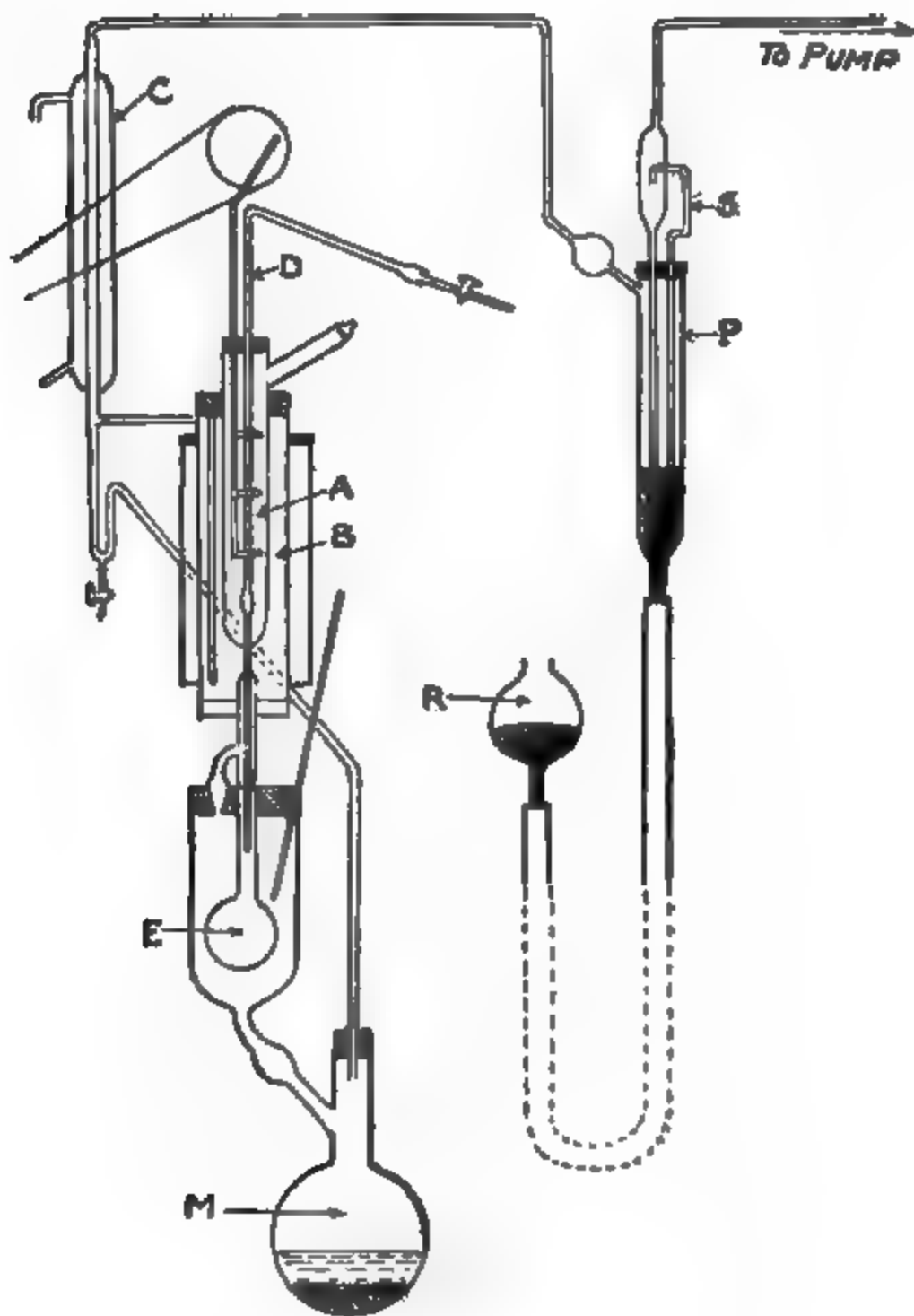


FIG. 189. Tyrer's apparatus for solubilities.

Although illustrations of special forms of apparatus designed for securing equilibrium in solubility determinations could be extended far beyond the number given, it is believed that the principal features have been made clear and it will no doubt be possible to adapt the devices here shown to many other cases for which accurate determinations of solubility may be desired.

**Separation of Saturated Solution from Undissolved Solid.** The next point, after the establishment of equilibrium between the solvent and solution, is the matter of successfully separating the saturated solution from the undissolved solid, preparatory to its analysis. There are, undoubtedly, many cases where this is a very serious problem. This is especially so for extremely soluble compounds, which yield viscous solutions as well as for those which do not readily settle out of the solution or cannot be removed by ordinary filtration. It is, of course, necessary to maintain the mixture at the temperature at which saturation was obtained until the complete separation of the solution and solid has been effected. The operation should, therefore, as a general thing, be conducted in the same bath used for preparing the saturated solution. Several forms of apparatus designed for this purpose are shown in the diagrams given in the preceding pages. For solutions which can be readily separated from the undissolved solid, a graduated pipet to which a stem with a plug of filtering material can be attached and which is adapted to being easily weighed, is the most convenient.

**Analysis of the Saturated Solution.** The weight of a known volume of the perfectly clear solution, that is, its specific gravity, should always be determined. This weighed quantity of solution, or a known dilution of it, furnishes a very convenient sample for the determination of the amount of dissolved compound.

In regard to the analysis, the procedure must be selected entirely on the basis of the number and character of the constituents present. In cases of the solubility of single non-volatile compounds, in solvents which can be more or less easily removed by volatilization, the plan in most general use is the evaporation of a known amount of the solution to dryness and weighing the residue. Special forms of apparatus to be used for this purpose have been proposed from time to time. These are, usually, vessels with tubular openings, arranged so that a current of dry air can be drawn over the surface of the heated sample.

In the case of solubility determinations in which the saturated solution contains more than one dissolved compound, the application of the usual gravimetric or volumetric procedures will, of course, be necessary.

In certain cases, where the direct determination of the amount of the dissolved compound present in the solution would be very difficult or impossible, an indirect method can sometimes be used. For this purpose, a carefully weighed amount of the compound must be used, and, after the period of saturation, the undissolved residue is filtered off under conditions which reduce losses to a minimum and, after drying to its original condition, it is weighed, and the amount which has been dissolved found by subtracting the weight of the undissolved residue from the quantity originally present.

**Identification of the Solid Phase.** The solubility of a compound, which is capable of existing in several forms, depends upon the particular form in which it is present in contact with the saturated solution. The question of the composition of the solid phase is, therefore, of considerable importance for the accurate determination of solubility. Although the identification of the solid phase presents little difficulty in the majority of cases, it sometimes happens that it can be made only by a more or less indirect method. The principal

reason for this is that adhering solution can usually not be completely removed from the solid phase and the analysis, consequently, does not give direct information of the required accuracy.

A method which has been used considerably for identifying the solid phase is that known as the *residue method* of Schreinemakers (1893). It is based on the principal that if an analysis is made of both the saturated solution and of a mixture of the saturated solution and the solid phase of unknown composition, the two points so obtained, when plotted on a coördinate system, lie on a line connecting the point representing the composition of the solid phase and the solubility curve of the system. Similar analyses of another saturated solution of the system and of its mixture with the solid phase, locate another such line. Since all lines so determined when extended, pass through the point representing the composition of the solid phase, their intersection locates this point definitely.

Although the original description of this method by Schreinemakers was illustrated by an example drawn on the rectangular system of coördinates, it has been used much more extensively, in a practical way, in connection with the later developed equilateral triangular diagram. In this case, each apex of the triangle represents one of the three components of the system, each point on a leg, a mixture of two, and each point within the triangle a mixture of all three components. When a number of saturated solutions are analyzed, the results correspond to points on the solubility curve of the system. If now some of the solid phase with adhering solution is removed from each mixture and analyzed, it is evident that the results thus obtained, being for samples made up of both the saturated solution and the solid phase, give points which lie on lines connecting the two. The points on the curve for the pure saturated solutions being known, it is necessary only to connect them with the points for the corresponding mixtures of solid phase and saturated solution, and to prolong the lines to their common intersection. This will necessarily be at the point representing the composition of the pure solid phase.

In applying the residue method of Schreinemakers, if the intersecting lines which fix the point corresponding to the solid phase meet at a very narrow angle, definite information as to its composition may not be secured. For cases such as these, a procedure to which the name "*tell-tale*" method was given by Kenrick (1908) and which is described in detail by Cameron and Bell (1910), has been developed. This method consists in adding to the mixture a small amount of an entirely different compound which remains wholly in the solution. After equilibrium has been reached, a portion of the saturated solution and of the solid phase with adhering solution are analyzed, and the quantity of the added "*tell-tale*" compound in each determined. From the result, showing the concentration of the added compound in the saturated solution, and the amount of it found in the mixture of solid and solution, the quantity of solution in contact with the solid can be calculated. Since the composition of the solution is also known, the difference between the composition of the solid plus solution and of the amount of solution known to be present, is the composition of the pure solid.

**Transition Temperatures** can frequently be accurately determined by relatively simple means, and since such data are useful in establishing fixed points on solubility curves they are valuable adjuncts to directly determined solubility data.

**Synthetic Method.** The procedures which have, so far, been mentioned are all classed as analytical methods of solubility determination. In contradistinction to these is the equally useful reverse process, by which the solvent and solute are brought together in previously measured quantities and the temperature ascertained at which the solution is saturated. To this procedure the designation synthetic method of solubility determination has been applied. One of the earliest investigators to use this method extensively was Alexejeff (1886) and it is, therefore, frequently referred to as the Alexejeff synthetic method of solubility determination.

The synthetic method can, of course, be used both for the solubility of solids in liquids and for liquids in liquids, but it is in the latter case that it is of greatest service. Its points of superiority, particularly in the case of the reciprocal solubility of liquids, are that the upper limits of the determinations can be extended far beyond the boiling point temperature and are, in fact, limited only by the resistance of the glass to pressure or to the action of the liquid. Only small quantities of the solute and solvent are required for a determination. It is applicable to compounds for which quantitative methods of analysis are not available or are of a tedious character. The mixtures, being contained in sealed tubes, are not subject to the action of constituents of the air, nor are losses, due to volatilization, to be feared. Although, in the case of solids, difficulties incident to the supersaturation, resulting from failure of the crystals to separate on cooling, are encountered, with liquids the point of saturation is made instantly and strikingly evident by the beginning of opalescence or clouding which occurs, and errors due to supersaturation are rarely encountered. A sure criterion that supersaturation does not occur rests on the observation of the temperature at which the cloudy solution again clears. If this temperature coincides with the temperature of the beginning of opalescence, it is certain that supersaturation has not occurred. The observation of the temperature of saturation can be repeated as often as desired, and the accuracy of the determination is ordinarily limited only by the care taken in making it.

The limitations of the method, aside from the supersaturation which may occur in the case of solids, are principally those resulting from the low temperature coefficients of solubility possessed by certain compounds, and which usually occur in the vicinity of maxima or minima of solubility curves. Although a "critical clouding" occurs in the vicinity of the so-called critical solution point, this possesses a characteristic appearance which is easily distinguishable from the clouding observed at the saturation point, and errors of observation due to it are not to be apprehended. In fact, it has been pointed out that supersaturation disappears at the critical point, and the synthetic method is ordinarily very accurate in the vicinity of the critical solution temperature.

Since, by the synthetic method the results are necessarily obtained under different pressures, this question has been given consideration from the theoretical and the practical side. Although it is possible that extremely high pressures would exert an influence, the conclusion appears justified that under

ordinary conditions, in which pressures of 10 atmospheres are not exceeded, no notable effect would be produced. The solubility curves obtained by this method do not show any abnormalities due to this cause.

In the case of the determination of the solubility of solids by the synthetic method, the operation consists in preparing a mixture of a carefully determined amount of the solvent and of the solid, and subjecting it to gradually increasing temperature and to constant agitation, while a continual observation of the changes taking place in the solid is made. When all but a few small crystals have dissolved, the change in temperature is regulated much more carefully and note is taken of the point at which the edges of these final crystals begin to change from sharp to rounded, or vice versa, or where the sizes of the particles visibly increase or diminish. Care must, of course, be taken not to allow the last portions of the solid to dissolve; otherwise, on cooling, considerable supersaturation may occur before the solid begins to separate from solution. The method is, naturally, most serviceable where the change in solubility with temperature is considerable, and where convenient methods for the direct analysis of the solution are not available.

The procedure of a determination in the case of the reciprocal solubility of liquids consists in introducing by means of capillary funnels weighed amounts of the two liquids into small glass tubes and sealing the ends. The amount of air space in the tubes should be kept low. Many convenient devices for weighing and introducing the liquids have been described. In the case of very volatile liquids it may be necessary to introduce them in thin walled bulbs, which can be broken after the tube containing the mixture has been sealed. The tube is then placed in a large beaker of water, or higher boiling liquid if necessary, and heat applied until the contents of the tube, on being shaken, become homogeneous. The temperature is then allowed to fall very slowly and an observation made, while the tube is constantly agitated, of the temperature of first appearance of opalescence. This observation can be repeated as many times as desired and the temperatures of appearance and disappearance of the clouding, which usually differ by only a few tenths of a degree, can be ascertained with certainty.

Since, by the synthetic method the data are for irregular intervals of temperature, in order to obtain results for a particular temperature it is necessary to plot the several determinations on coordinate paper and from the solubility curve so obtained, read the value for the temperature in question.

**Freezing-point Method.** A modification of the synthetic method, which is applicable particularly to solutions which contain relatively large amounts of the dissolved compound, is that which consists in a determination of the freezing-point of the mixture. This point is, in fact, the temperature at which the separating solid compound is in equilibrium with the solution.

The difference between the freezing-point determination and the observation of the point of growth or diminution of a crystal in a liquid is that, in the former, the establishment of equilibrium is recognized exclusively by the change of the thermometer. The solution is cooled gradually, during which the thermometer sinks slowly to a point below the freezing temperature. As soon as the first crystal appears, either spontaneously or by intentional introduction (seeding), the thermometer rises suddenly to the freezing-point and remains stationary for some time.

This method can, of course, be used in a large number of cases for the determination of solubility. Those portions of the solubility curves of salts in water for which ice is the solid phase, are practically always determined in this way and it may be said, in general, that for determinations made at low temperatures, the freezing-point method is to be selected whenever possible.

For the practical execution of the method the very well known apparatus of Beckmann is most convenient and satisfactory. The determinations must, of course, be made with all the refinements which have been developed for accurate freezing-point measurements.

The method has been used extensively for the discovery of addition compounds. Its use for this purpose is based upon the principle that if to a pure compound, *A*, a second, *B*, is added, the freezing-point of *A* is lowered; similarly the freezing-point of *B* is lowered by *A*, and the two descending curves thus obtained intersect at the eutectic. If, however, a compound, *A<sub>2</sub>B*, is formed, this also acts as a pure substance and its freezing-point is lowered by either *A* or *B*. Hence the freezing-point lines do not meet at a single eutectic but exhibit in this case a maximum, the position of which indicates the composition of the compound.

**Volume Change Method.** Still another method, which is a modification of the synthetic, is that designed to indicate the reciprocal solubility of liquids by a determination of the volume changes which occur when two relatively sparingly miscible liquids are shaken together in a closed vessel. The apparatus consists usually of a cylindrical receptacle which is provided with a constricted graduated section either at one end or near the middle. Such volumes of liquids are chosen that the meniscus separating them lies in the constricted graduated tube. The determination consists in superimposing measured volumes of each liquid and noting the position of the meniscus before and after a period of shaking at constant temperature. From the increase or decrease of volume of the two layers, as estimated from the change in position of the meniscus, the reciprocal solubility of the two liquids is calculated. It is to be noted, however, that the solubility of liquids is in practically all cases reciprocal, and without an analysis of the two layers the true solubility can not usually be deduced.

**Titration Method.** A special case of the reciprocal solubility of liquids is that representing equilibrium in ternary systems yielding two liquid layers. Such equilibria are usually determined by relatively simple titration procedures, but for the interpretation and description of the results, special terms have been developed and these require more or less detailed explanation.

When a third liquid is added to a mixture of two others which are miscible to only a slight extent, the added liquid, if soluble in each of the others, will distribute itself between the two and an equilibrium will be reached. If the two layers are then analyzed and the results plotted on coordinate paper, two points, corresponding to the two layers, will be obtained. If more of the third liquid is added, equilibrium will again be established after a short period of shaking and the analysis of the two layers, to which the designation *conjugate* layers has been given, will fix two more points when plotted on the coordinate paper. The process may be repeated until a considerable number of points have been obtained. When this has been done, it will always be found that these points are the locus of a smooth curve, to which the designation *binodal* curve has been given. If the pairs of points corresponding to the conjugate

layers are connected, the lines so obtained are defined as *tie lines*. Since it is evident that with the continued addition of the third or *consolute* liquid, a point must finally be reached at which the resulting mixture will no longer separate into two conjugate layers, the tie lines successively determined as above described, will become shorter and shorter until finally the last one is reduced to the point corresponding to the homogeneous mixture of the three components. To this is given the name *plait point*.

Although for the above example a ternary system made up of three liquids has been taken, there are a large number of salts and other solid compounds which, when dissolved in mixtures of liquids of certain concentrations, cause the latter to separate into conjugate liquid layers. These systems have aroused much interest from time to time and considerable data for them are given in the literature.

Since it is usually difficult and frequently impossible to analyze directly a homogeneous mixture of liquids, and thus determine the points on a binodal curve, a simple titration method for this purpose has come into general use. By means of this a homogeneous mixture of known amounts of two of the components is titrated with the third just to the point of initial separation of the second layer, which is usually very sharply indicated by the appearance of clouding or opalescence. The procedure may also be reversed and the consolute liquid added just to the point of clearing of the cloudy mixture of the other two. By this plan the synthetically derived composition of one of the two conjugate layers and thus of one point on the binodal curve is known. The determination of the tie line and therefore, the identification of the corresponding point on the curve for the conjugate liquid, requires an additional experiment for its location. Several procedures for this purpose have been developed. They usually depend upon the determination of one or more constants of specially prepared pairs of conjugated liquids, such as their specific gravities or refractive indices. In the case of mixtures of which one member can be easily determined analytically, tie lines can be located by the quantitative determination of this member in pairs of conjugated liquids.

In general, the titration method for the determination of the solubility of liquids is applicable to many cases. The facts, that equilibrium is attained so promptly in liquids and that the evidence of the appearance of a second insoluble layer is usually so striking, make it of great value. Refinements have been introduced such as the addition of liquid or solid dyes to the mixture in order to facilitate the detection of the end point, and the development of particular forms of apparatus for measuring and weighing the liquids. The constituents of the mixtures are usually weighed but the volume relations and, therefore, the specific gravities can also be approximately estimated, by using graduated vessels for making the titrations, and measuring in them the volumes of the final mixtures.

As a usual thing the temperature coefficients are not very great in the case of liquid mixtures and the very accurate control of the temperature is not imperative. When such control is necessary, however, the use of a thermostat does not seriously complicate the determination.



**Distribution Coefficients.** As mentioned above, when a third compound is added to a mixture of two liquids which are relatively immiscible, it will dissolve to a certain extent in each and the composition of the two layers represent conjugate points on the binodal curve for the system. The results are, however, of interest from another point of view, namely that of the distribution of the compound between the two solvents. This distribution coefficient is, in many cases, of considerable interest in connection with analytical methods based on shaking out procedures and also in connection with such problems as the molecular state of compounds in solution, their dissociation and other points of theoretical interest. Distribution coefficients have, therefore, been studied to a large extent and much data for them are available. In general, the determinations are made by relatively simple methods. The amount of the compound present in a definite amount of each layer, after equilibrium has been established by adequate agitation, is determined in any manner most convenient. If the total amount of solute is known, and that found in one layer, the amount in the other can, of course, be calculated by difference. The results are usually expressed on the volume basis, since it is the ratio of the amounts present in the same molecular state in equal volumes of the two layers which is a constant, independent of temperature and concentration.

It is evident that when the concentration at the saturation point is considered, the amount of the compound which enters each layer depends upon its solubility in the liquid, consequently the distribution coefficient is the relation of the solubilities of the dissolved substance in the two solvents. Variations from this, aside from changes in molecular state, etc., in one or the other solvent are due to such causes as the reciprocal solubility of the so-called immiscible solvents, which will, of course, be influenced by the presence of the dissolved compound, especially at the higher concentrations. Variations of the coefficient with temperature would result in cases where the solubilities of the compound in the two solvents do not change at the same rate with temperature.

**Electrolytic Conductivity Method.** Of the physical properties which can be used for the determination of the concentration of a solution, such as specific gravity, refractive index, etc., the electrolytic conductivity is of particular value in the case of those very sparingly soluble compounds which yield solutions too dilute to be analyzed by gravimetric or volumetric methods. By its use the progress of the saturation can be followed without separating the undissolved solid from the solution, or even removing the portion used for the determination. The special electrical equipment which is required, however, and the need for water of exceptional purity and of vessels of particular qualities, restrict its general use.

The method of calculating the concentration from the conductivity is based on the assumption that at the very great dilutions involved, complete dissociation occurs. Therefore, the limiting value to which the equivalent conductivity approaches at infinite dilution is, for practical purposes, attained, and  $\Lambda = \Lambda_{\infty} = l_a + l_k$ , where  $l_a$  and  $l_k$  are the ionic conductivities of the anions and kations. These values are known for all the principally occurring ions. The observed specific conductivity  $\kappa$  is, however, connected with the equivalent conductivity and the concentration  $\eta$  by the equation  $\Lambda = \kappa/\eta$ , in which  $\eta$  represents the concentration in gram-equivalents per cubic centimeter. Rearrangement and substitution give  $\eta = \kappa/(\Lambda_{\infty})$ . From this equation the solubility

of the substance under investigation is calculated by substituting the measured specific conductivity of the solution and the known values of the ionic conductivities.

**The Solubility of Gases in Liquids.** When a gas and a liquid are intimately mixed by shaking, a definite amount of the gas will be dissolved by the liquid and, simultaneously, the vapor of the liquid will mix with the gas in the space above the liquid. The partial pressure of the liquid in the gas space is almost exactly the same as that of the pure liquid at the solution temperature, since the influence of the relatively slight amount of dissolved gas is insignificant in by far the most cases. The amount of gas which is dissolved depends both on the nature of the gas and of the liquid and is, furthermore, a function of the temperature, and pressure.

In regard to the influence of pressure, the absorption law of Henry holds for the most part, when the gas solubility is not too great. According to it, the amount of pure gas, which is taken up at constant temperature by a given amount of liquid is proportional to the pressure of the gas.

The temperature acts almost always in the sense that the solubility decreases as the temperature rises.

The solubilities of gases are usually expressed either in terms of the Bunsen "Absorption Coefficient"  $\beta$ ,<sup>1</sup> or the Ostwald "Solubility Expression"  $l$ .<sup>2</sup>

The experimental methods for the determination of the solubility of gases vary according to the nature of the gas. For those which dissolve in relatively large amounts and can be analytically determined with accuracy, the saturated solution may be analyzed by ordinary quantitative methods. Thus, in the case of the solubility of sulfur dioxide in aqueous solutions of salts, the solutions were saturated by passing a stream of the gas through them at atmospheric pressure and, when equilibrium was attained, a measured portion of the solution was withdrawn, transferred to an excess of standardized iodine solution and the excess of the latter titrated with thiosulfate. A gravimetric procedure was used by Christoff (1905) for the determination of the solubility of carbon dioxide in aqueous salt solutions. In this case the solutions were weighed before and after the passage of the gas through them and the increase in weight, after applying necessary corrections, taken to represent the solubility at the temperature of the experiment and at atmospheric pressure. The absorption flasks were of special shape and the gas was previously passed through a series of U tubes, containing the same aqueous solution, in order to prevent loss of water from the experimental solution which, otherwise, would have occurred.

<sup>1</sup> $\beta$  = the Bunsen Absorption Coefficient which signifies the volume ( $v$ ) of the gas (reduced to 0° and 760 mm.) taken up by unit volume ( $V$ ) of the liquid when the pressure of the gas itself minus the vapor tension of the solvent is 760 mm.

$$\beta = V \left( \frac{v}{1 + 0.00367 t} \right)$$

<sup>2</sup> $l$  = the Ostwald Solubility Expression which represents the ratio of the volume ( $v$ ) of gas absorbed at any pressure and temperature, to the volume ( $V$ ) of the absorbing liquid, i.e.  $l = \frac{v}{V}$ . This expression differs from the Bunsen Absorption Coefficient,  $\beta$ , in that the volume ( $v$ ) of the dissolved gas is not reduced to 0° and 760 mm. The solubility  $l$  is therefore the volume of gas dissolved by unit volume of the solvent at the temperature of the experiment. The two expressions are related thus:

$$l = \beta (1 + 0.00367 t), \quad \beta = \frac{l}{(1 + 0.00367 t)}$$

In the great majority of cases, however, gas solubility is determined by a method based upon the measurement of the volume of the gas absorbed. The apparatus consists essentially of an absorption flask for the liquid, connected by means of a tube of small bore to a graduated buret in which the gas is measured above mercury, the level of which can be altered by raising or lowering a container connected with the buret by means of a rubber tube. Many forms of this apparatus have been described and the disadvantages of the earlier forms have gradually been remedied. A relatively simple form of this appar-

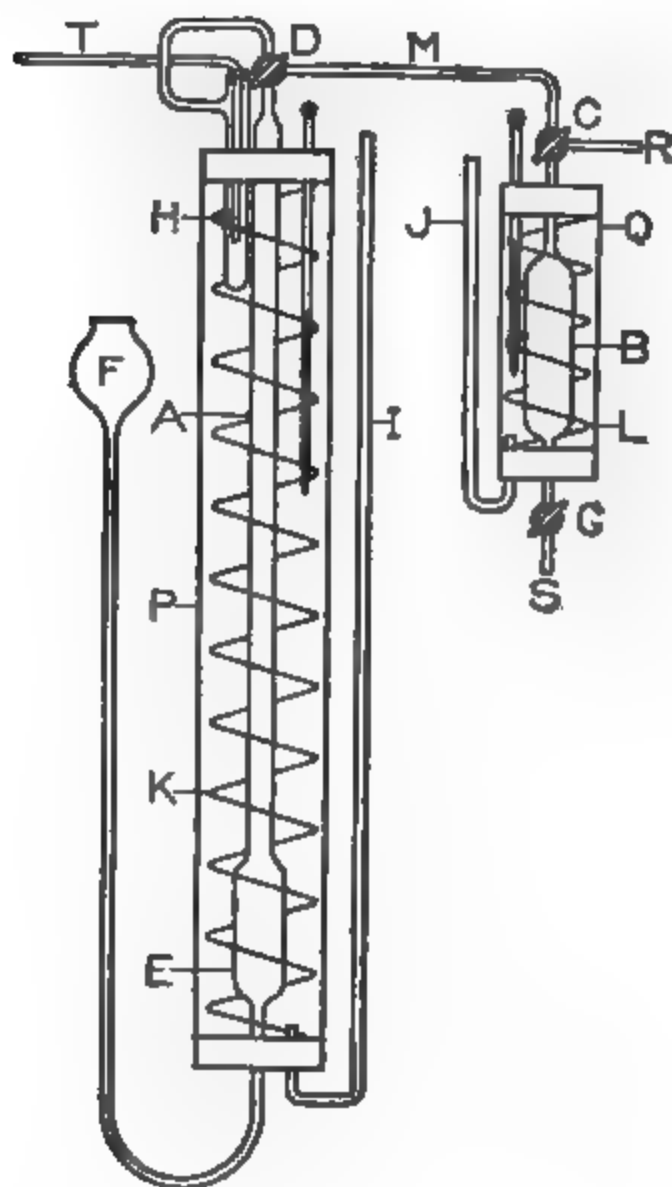


FIG. 190. McDaniel's apparatus for determining gas solubilities.

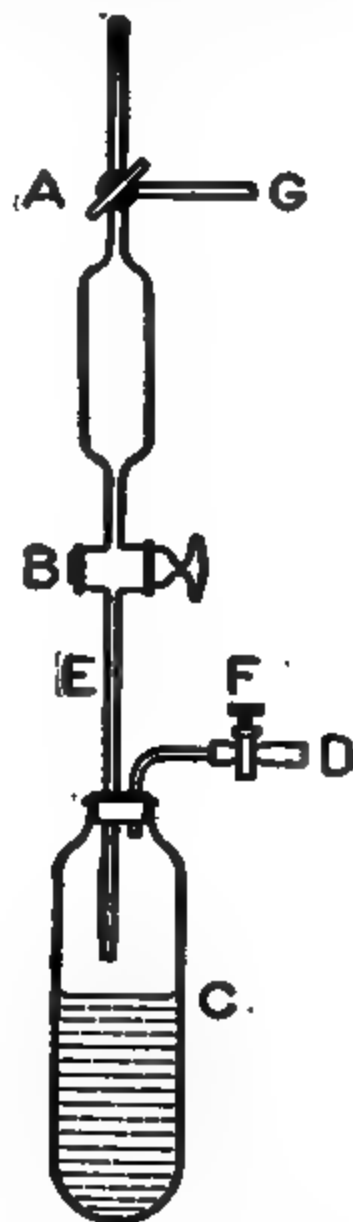


FIG. 191.

atus, but one which embodies the essential features required for accuracy, is that described by McDaniel (1911) for the determination of the solubility of methane, ethane and ethylene in a large number of organic solvents at various temperatures.

This apparatus is shown in Fig. 190. A is an ordinary gas buret and B an absorption pipet of the form first used by Ostwald. "The buret and pipet are connected by means of the glass capillary M sealed directly onto each, so that the whole forms one solid piece of glass apparatus *without rubber or cement connections of any kind*; thus any possibility of leaks from these extremely troublesome sources is entirely avoided. The whole apparatus is clamped solidly to a rigid support so that it can be taken up in the hands and shaken

for the purpose of bringing the gas into intimate contact with the liquid. The pipet and buret are each provided with a three-way stopcock, *C* and *D*. These can be turned in such a way as to allow the gas to sweep out the air from the connecting capillary. By the same means the two vessels may also be connected directly with each other as well as separately with the outside air or source of gas supply. The pipet and buret are each provided with a water jacket, *P* and *Q*. The temperature of each is regulated by means of the electrically heated coils *K* and *L*." These coils are of manganin wire and are connected in series. The rate of evolution of heat in the jackets was adjusted in the first place by varying the length of the manganin wire, until the temperature was the same in each jacket. Stirring was accomplished by blowing air through the tubes *I* and *J*. The differences in temperature between the pipet and buret were never greater than 0.1°.

In carrying out a determination by this method it is, of course, necessary that the solvent be completely free of dissolved air or other gas. This is perhaps the most important part of the determination and a special form of apparatus for the purpose is described by McDaniel (1911) and is shown in Fig. 191. "The liquid was boiled under diminished pressure in the flask *C* attached directly to the lower opening of the pipet by means of the rubber stopper as shown in the figure. Connection with the air pump is made at *D*. During the boiling the lower opening of the inlet tube *E* is above the surface of the liquid in *C*, the stopcock *B* being closed. When the air has been completely expelled, the screw pinchcock *F* is closed while the air pump is still in operation. The flask *C* is now raised until the lower end of *E* reaches nearly to the bottom of the flask. The air pump is now connected at *G* and the cock *H* opened so as to make connection with the pipet. *B* is now opened and the inflow of air through *D* regulated by gradually opening *F* in such a manner that the liquid is very slowly forced up into the pipet. In this manner the liquid never comes into contact with the air under full atmospheric pressure but only under greatly diminished pressure. The absorption of air under these conditions can only be inappreciable, especially since the liquid in the flask remains perfectly quiet, and only the lower portion is used."

Having filled the pipet *B*, Fig. 190, with the air-free solvent as just described, "*T* is connected with the source of gas supply and the cocks *C* and *D* are turned in such a way as to allow the gas to sweep out the air from the capillary, *M*. The buret is then filled in the usual manner by lowering the leveling tube *F*, the cock *D* having been turned so as to connect *T* with *E*. Care is taken to keep the entering gas under a slight pressure by keeping the mercury level in *F* slightly above that in *A*. This prevents air from entering through any leaks in the train connecting the gas generator with the buret." The gas must be completely saturated with the vapor of the solvent and this, with other than aqueous solvents, may require, in addition to drawing it through some of the solvent in *H*, that a thin layer be placed in the buret and time allowed for it to saturate the gas sample.

"After again allowing the current of gas to flow through the capillary *M* for a short time the buret and pipet are connected with each other by turning the three-way cocks *D* and *C* in the proper direction. The determination of the amount of absorption is then made as follows: A portion of the gas is passed into the pipet by raising *F* and opening *G*, the displaced liquid being caught in a graduated cylinder. The cock *C* is closed and the gas and liquid in the pipet brought into intimate contact with each other by shaking the whole

apparatus. *C* is now opened to allow gas to enter from the buret to replace that absorbed. This process is repeated until, on opening *C*, there is no further decrease in the volume of gas in *A*. The volume absorbed is found by subtracting from the original volume of gas, the volume remaining in the buret plus the volume in the pipet. The volume of gas in the pipet is equal to the volume of liquid drawn off. The volume of liquid remaining is easily calculated from the known volume of the pipet. The absorption coefficient or 'solubility' is the ratio of the volume of gas absorbed, measured at the temperature of the experiment, to the volume of the saturated liquid. It may be reduced to the coefficient used by Bunsen by dividing by  $(1 + \alpha t)$ ."

In the case of the majority of investigators who have used this method, particularly for determinations at high or low temperatures, the absorption pipet has been kept at the temperature of the experiment and the gas measuring buret at room temperature, the two being connected by means of a flexible capillary which permits the absorption pipet to be independently shaken. This arrangement makes it necessary, in calculating the absorption coefficients, to apply the usual corrections for temperature and vapor pressure to the volume of gas in the buret. This is a complication which in some cases causes uncertainties in regard to the accuracy of the results as finally calculated.

An apparatus designed for determinations at very high pressures, using a Caillet compression tube, is described by Sander (1911-12). It was used for determination of the solubility of carbon dioxide in water, alcohols, and other organic solvents. The principle involved is that the pure gas is first compressed above mercury in a graduated tube and the volumes corresponding to given pressures noted. Similar readings are then taken for the same gas after a small accurately measured amount of solvent has been introduced into the graduated tube. The difference between the two volumes at the same temperature and pressure, reduced to 1 kg. per sq. cm. and 1 cc. of liquid, represents the solubility of the gas in the given solvent.

Finally, attention should be called to the method of determination of gas solubility based on the principle that, for volatile solutes which obey the laws of Dalton and Henry, the amount which is carried away by an inert gas when known volumes are bubbled through solutions of known strength of volatile solute, can be used to measure the comparative solubilities in solvents of different concentrations. An example of this method is the determination of the solubility of ammonia in aqueous salt solutions by Abegg and Riesenfeld (1902). The very ingenious apparatus consists of a generator for developing a stream of  $H_2 + O_2$  from aqueous NaOH, by means of an electric current measured with the aid of a copper voltmeter, and the volume of gas thus determined. This was passed through a spiral in the vessel containing the ammonia solution of known concentration. The mixed gases passing out of this were received in a third vessel containing 5 cc. of 0.01 *N* HCl. Electrodes were provided in this vessel and, by means of conductivity measurements, the point determined at which all of the HCl became saturated with  $NH_3$ . Since the volume of the  $H_2 + O_2$  required for this purpose was known, the partial pressure of the  $NH_3$  in the mixture could be directly ascertained. Comparative determinations of the vapor pressure of the ammonia in water and a series of salt solutions made in this way were calculated to ammonia solubilities on the basis of the relation that, for two solutions of equal ammonia content, the ammonia pressure is reciprocally proportional to the solubility of the ammonia in them.

# STANDARD METHODS OF SAMPLING

J. B. BARNITT<sup>1</sup>

## GENERAL OUTLINE FOR SAMPLING SOLIDS

### Introduction

An accurate and uniform sampling procedure, applicable to all solid materials from the viewpoint of both producer and consumer, would necessitate the standardization of an infinite number of details, and probably result in a very cumbersome and impractical manipulation. It, therefore, appears advisable to first consider the various steps of the process of sampling, attempting their standardization and then applying this standardization to each particular product or group of related products.

The process of sampling is divided into three major operations:

1. The collection of the "gross" sample.
2. The reduction of the "gross" sample to a proper and convenient size for transportation to the laboratory.
3. The preparation of the sample for analysis.

These essential points and the accuracy with which they are performed determines the value of the subsequent analytical results. Experimental data and general mathematical deductions make it possible to standardize these operations with a fair degree of accuracy.

### Sampling Unit

The sampling unit may be defined as that portion of the material which is chosen in such a manner that there is a high probability that it will contain the different sized particles of the material in the proportion in which they occur in the entire bulk of the material. Providing there are no great uncontrollable irregularities in the material, the sampling unit, if taken under carefully prescribed conditions for each different class, should be properly representative of the material. However in order to obviate the necessity of specifying in great detail, and to guard against unforeseen sectional variations in the material, it is more expedient to select a number of sampling units, these depending upon the size of the shipment to be sampled, and combine these sampling units into one large sample called the "Gross Sample."

The character of the material, size of the various particles, uniformity of composition and the prominence of any one or more constituents are factors governing the determination of the amount to be taken as the sampling unit. Without considering a mathematical discussion of the modulus of precision of a condition which would be impossible of duplication and in view of the experimental data compiled on the sampling of coal, it is safe to adopt, as the general sampling unit, an amount of material equal to approximately 500 times the weight of the largest particle. If this is impractical, due to the presence of very large particles, and the material cannot be reduced by passing it through a crusher, it will be necessary to reduce, by hand, the large particles at the various sampling points so that the correct proportion of large particles can be included in the sampling unit. In some cases, however, a different bulk of sampling unit will be found necessary.

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### Collection of the Gross Sample

The amount of material to be included in the gross sample depends more upon the size of the individual particles than upon the size of the shipment since it is simply a multiple of the sampling unit. When the shipment is large and frequent sectional variations do not prevail, and, it is being transferred by containers with a capacity approximately equal to the sampling unit, it is advisable to take the entire contents of a definite percentage of the containers as increments of the gross sample.

When the accumulated gross sample is too large to handle conveniently as a unit, it is permissible to reduce the gross sample in small sections by the standard procedure and subsequently combine the reduced portions in the correct ratio.

#### 1. From Carload Lots

(a) **When the Material is to be Unloaded from Flat-bottomed Cars.**—Divide the top surface of the car into eight equal areas and, from each of these sections, take approximately the equivalent of one sampling unit in the following manner: From a stable bank of the material, beginning from the bottom, take with a shovel, at regular and equal intervals from the bottom to the top of the bank, ten equal portions of the material as specified. Combine these sampling units for the gross sample.

The stable bank may be obtained:

1. By digging down to the bottom of the car at the center of each section.
2. As the center of each section of the car is reached during the ordinary process of unloading by shoveling or otherwise.

(b) **When the Material is Being Transferred from or to the Car by Means of Wheelbarrows, Tram-cars, Wagons, Etc.**—Take the specified increment according to the material in question from a specified number of conveying containers. Combine these increments for the gross sample. When at any point a particle is encountered which is larger than the specified increment it should be broken down and a portion of it included in the sample.

(c) **When the Material is Dumped from a Hopper Car into a Hopper, Bin or Pile.**—Under these conditions, the sample is taken from the resulting cone-shaped pile by beginning at the bottom outer edge of the pile and taking the specified increment, according to the character of the material, every two feet on a straight line to the apex of the cone. This operation is repeated on each quadrant of the pile. The entire procedure is repeated after each car has been dumped and all increments combined for the gross sample.

#### 2. From Wheelbarrows, Barrels, Bags, Tram Cars, Carts, Trays, Etc.

(a) From a specified number of containers, take the specified increment and combine them for the gross sample.

(b) Take the entire contents of every  $n$ th container and combine them for the gross sample.

(c) If the material is fairly uniform and composed of small particles, sample the container by taking ten equal specified increments uniformly distributed on two right angle diagonals across the surface of the container. Sample the

specified number of containers in this way and combine the several portions for the gross sample.

### **3. From Crane Buckets, Cars, Carts and Similar Containers, Chutes, Etc.**

(a) If one container amounts to less than one sampling unit, take every 10th load and combine these for the gross sample.

(b) If one container amounts to approximately 1-3 sampling units, take every 20th load and combine these for the gross sample.

(c) If one container amounts to more than three sampling units, take every 50th load and combine these for the gross sample. Note: When very large shipments are being sampled by the above procedures very large gross samples will result which would be difficult or inconvenient to reduce to the laboratory sample. In this case the gross sample may be reduced periodically as follows. At regular intervals, representing a definite number of tons, the gross sample is quartered, one quarter reserved and three quarters returned to the main bulk. The total combined quarters thus reserved are mixed by shoveling into a cone shaped pile and then further reduced by the Standard Procedure to the laboratory sample.

(d) When the material is composed of particles one inch or less in size, take a specified increment from every  $n$ th container.

(e) When the material is being dumped into a crusher from which it flows or is flowing, from a drying kiln or other process kiln, the material may be sampled by taking specified increments from the outflowing stream at stated regular intervals.

### **4. From Shipholds, Scows, Hoppers, Hopper-cars, Bins, Storage Piles, Etc.**

In this case the material may be sampled in any of several ways.

(a) According to the previous section 3, while loading or unloading.

(b) According to the section 1, for carloads while unloading or loading.

(c) While using material from a storage pile, daily or periodic samples may be taken as follows: On ten vertical lines from the bottom to the top of the face of the pile distributed at uniform distances across the face, take ten equal specified increments at equal distances from bottom to top. Combine these increments for the gross sample over any desired period.

### **5. For Powdered Material**

When the material is a fine powder or is composed chiefly of material under 2 mm. and contains a small amount of unsegregated particles up to 10 mm. in the largest dimension, the sampling unit is taken by means of a specially designed thief (Fig. 192-1) or by means of a suitable shovel, dipper, etc.

(a) From large shipments, as shipholds, scows, barges, cars, etc. On a line through the center of the holder lengthwise, take portions with the thief every five feet. Repeat this operation on each of two lines parallel with and half way between the first line and each side of the holder. Combine all the portions for the gross sample. If the shipment is composed of more than one holder, combine the portions from each holder into a composite gross sample.



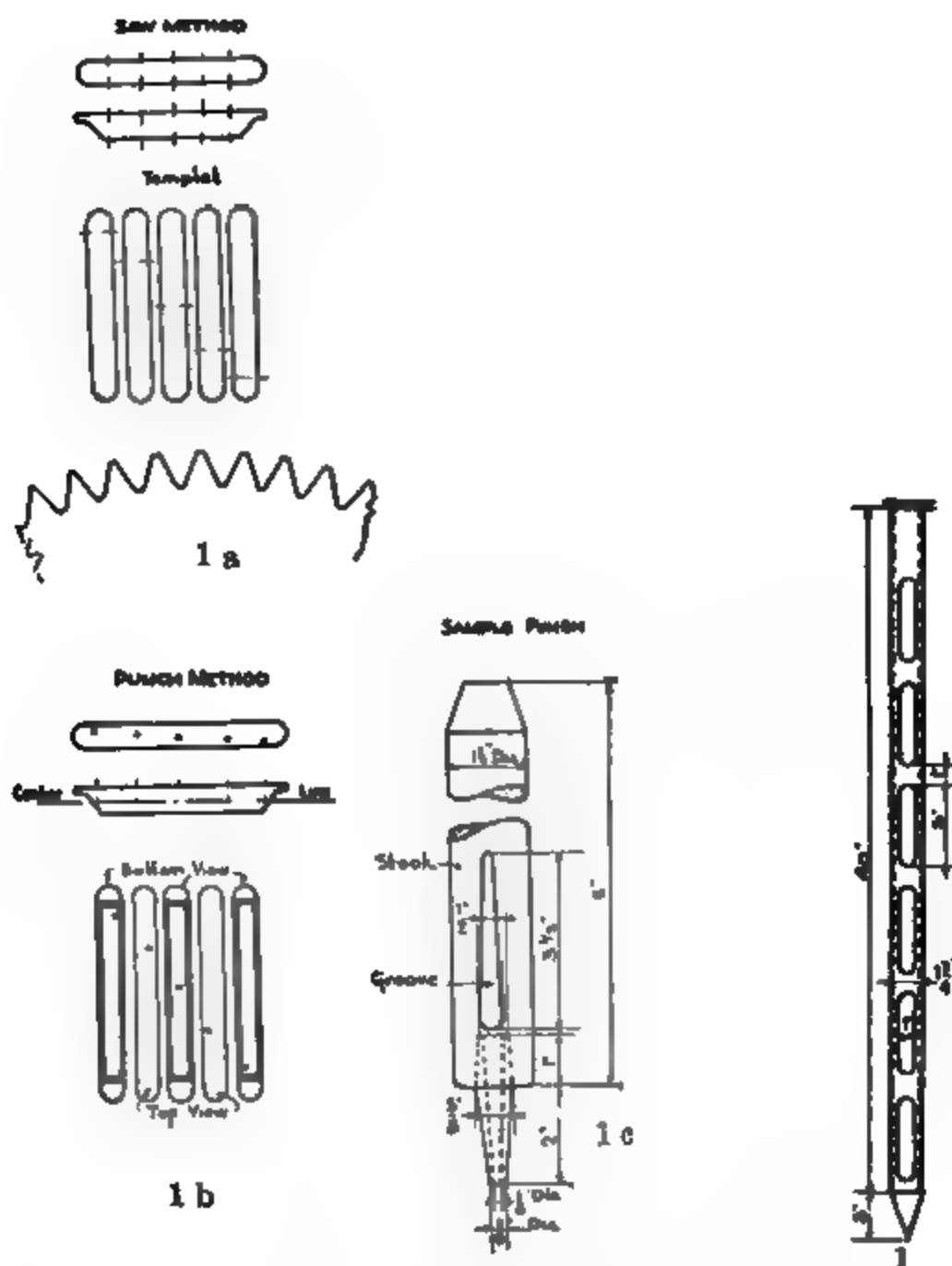


FIG. 192. Apparatus for Sampling Solids.

Sect. 1. Thief for sampling solids  $\frac{1}{8}$ " diameter or smaller. Openings to correspond. Both tubes hollow and to be made from  $\frac{1}{8}$ " sheet brass (hard). Inside tube to fit snugly into outside tube. Point to be steel or iron.

Sect. 1a. Saw Method of Sampling Pigs. The bars are sampled in sets of five, according to Template as shown. Saw is sharpened on Emery Wheel to size and shape here shown.

Sect. 1b. Punch Method of Sampling Pigs. The bars selected as samples are placed in a line, with every other bar, bottom side up. The sampling is done according to template in sets of five bars each, as indicated above. The punch must be driven through the bar. If a large sample is desired, the bars are turned over and sampled on the other diagonal.

Sect. 1c. Sample Punch.

(b) From tram cars, carts, buggies, etc.

Take a specified portion from each holder with the thief or shovel and combine all portions for the gross sample.

(c) From barrels, bags, wheelbarrows, etc.

Take a portion from every  $n$ th container and combine the portions for the gross sample.

(d) From small piles (not more than six feet in height).

With the thief, take one portion vertically at the peak of the pile and one vertically at each of ten points uniformly distributed along a line around the pile half-way between the peak and the edge of the pile. Combine these portions for the gross sample.

(e) From a well-mixed bulk of material (from mixers, packing machines, etc.).

After allowing a specified quantity, according to the condition of the material and type of apparatus, to flow past the sampling point, take the specified quantity for a sample. Periodic samples may be taken in the same manner, as often as desired.

#### 6. From Wet Material

Wet materials arrange themselves in several classes:

When the material is thoroughly wet but not dripping, take the sample by any of the foregoing suitable procedures, keeping the collected portions in moisture tight containers.

(b) When water is dripping from the material, take the sample as prescribed for the particular material by one of the foregoing procedures and allow the total gross sample to drain, the drainage and remainder of the sample being weighed and recorded. If further elimination of water is necessary either by air drying, artificial drying or pressing, before the gross sample is reduced to the laboratory sample, the total water eliminated must be calculated and taken into account in the final evaluation of the material to the original wet condition. In case this water carries some of the material in solution, it will be necessary to ascertain the amount of this by analysis and include the results in the final evaluation.

(c) When fine solid material is non-uniformly suspended in a liquid several vertical sections of the material may be taken by means of a specially designed thief and combined for the gross sample. (See general outline for sampling liquids.)

#### 7. From Hygroscopic or Deliquescent Materials

(a) When such material is contained in airtight containers which may be readily opened and closed, take a sample by means of a thief (Sect. 1), when the material does not contain resistant particles, larger than  $\frac{1}{2}$  inch in cross section or, otherwise, by means of a small scoop or shovel. These increments should be placed and retained in an air-tight receiver until ready for the analysis.

(b) When such material can be sampled while being transferred to the final container for shipment, small and equal increments at uniform and regular intervals, are taken directly from the stream by means of a suitable dipper and combined for the gross sample.

### 8. From Kilns, Roasters, Dryers, Furnaces, Etc.

This class of material constitutes a special case, and, consequently the size of sampling unit and manner by which it may be taken will be specified according to the size of particles and character and condition of the material.

### 9. Sampling Non-ferrous Metals and Alloys

(a) **In the Form of Pigs, Billets, Ingots, Rolls, Slabs, Etc.**—One pig, etc., should be taken to represent each ton of metal in the lot and each of these should be sampled by one of the following methods after thoroughly cleaning the surface to be sampled.

1. By sawing completely through the specimen as illustrated by Sect. 1a, Fig. 192. The sawdust from all the specimens is then thoroughly mixed and quartered down on a clean surface and the required amount of sample drawn.

2. By punching or drilling completely through if the equipment permits, or halfway through from two opposite sides as illustrated by Sect. 1c, 1b, Fig. 192. In this case the holes shall be spaced along a diagonal line from one corner of the specimen to the other. Sampling in this manner may be so arranged that one or more holes are made in each of several specimens of a group in such positions that they represent consecutive positions on the diagonal of a single specimen. (See illustration in Sect. 1c.) These punchings or drillings are carefully melted in a clean graphite crucible, and either granulated by carefully pouring into distilled water and thoroughly drying, or by casting into thin slabs which may be sawed completely through in several places and the sawdust treated as described above. Drillings may be chipped and mixed if convenient.

(b) **In the Form of Sheets.**—In sampling brass discs, and sheets, when they can be crated so that the edges are flush, recourse can be made to a portable milling machine operated by a  $\frac{1}{4}$  H.P. electric motor run transversely across the edges, so adjusted that only a very thin milling is taken from each disc or sheet. These are coned and quartered for the sample. By this method the serviceability of the disc or sheet is not destroyed, and the completeness of the sampling depends only on the accuracy of adjusting the edges in the crate.

### Procedure for Reducing the Gross Sample

By combining the several sampling units, the gross sample is obtained which should now be so large that large single chance particles of material could be entirely foreign matter or entirely pure substance and affect only slightly if at all the final sample. Increasing the size of the gross sample increases its accuracy, but cost and convenience of collection and reduction of sample, limit the degree to which this can be carried to advantage. The reduction of the gross sample to the laboratory sample is an operation which must be performed with accuracy and precision. Automatic machinery and labor and time saving devices may be used for this operation adhering closely to the following general scheme with the exception that some materials of uniform composition need not be finally reduced as small as 6 mm.—4 mesh—while it may be necessary to finally reduce other material to .14 mm.—100 mesh—or finer.

In sampling large shipments, the gross sample may become excessively large and unwieldy. This may be obviated by periodically reducing the gross sample by the Standard Long Pile and Alternate Shovel Procedure, and subsequently compositing these reduced portions for the final gross sample.

### Reduction of the Gross Sample

(Approx. 1000 lbs.) crushed to about 22.6 mm.—1 mesh; thoroughly mixed and halved by the Long Pile and Alternate Shovel procedure.

- Discard* One-half crushed to about 16 mm.—1.5 mesh; mixed and halved by  $\frac{1}{2}$  the Long Pile and Alternate Shovel procedure.  
 $\frac{1}{2}$  One-half crushed to about 11.3 mm.—2 mesh; mixed and halved by the Long Pile and Alternate Shovel procedure.  
 $\frac{1}{2}$  One-half crushed to about 4 mm.—5 mesh; mixed by rolling on canvas; halved by Cone and Quartering procedure.  
 $\frac{1}{2}$  One-half ground to about 2 mm.—10 mesh; mixed by rolling on canvas; halved by riffing (or sampling machine) or by the quartering procedure.  
 $\frac{1}{2}$  One-half mixed and riffled down to about 8 lbs.

The entire eight pounds is then further reduced and the required sample taken according to the character of the particular material.

A portion for the determination of moisture may be taken at some point during the reduction according to the character of the sample and manner in which the moisture test is made. When a moisture sample is wanted it is necessary that the sampling units be collected and stored under conditions whereby moisture would not be lost or absorbed. The mixing, crushing and halving operations, preceding the taking of the sample for moisture should be accomplished as rapidly as possible.

In case the gross sample contains an excessive amount of water which would be lost in the subsequent operations necessary to reduce it to the laboratory sample, it should be kept in a tight container during the collection of the various increments, after which it is weighed and allowed to air-dry, or it may be dried artificially, and reweighed. It is then in a condition to be reduced to the laboratory sample according to the above scheme, taking into account, of course, the moisture thus driven off from the original gross sample in the final calculation for the evaluation of the material.

### Reduction of Gross Sample (Long Pile and Alternate Shovel)

This procedure is based upon the method recommended and used by the U. S. Bureau of Mines.

1. Thoroughly mix the entire gross sample, after crushing in a suitable manner until all pieces are approximately one inch or less in any dimension, by shoveling it into a cone-shaped pile, depositing each shovelful on the apex of the pile. (Fig. 193, A and B.)

2. Shovel all of the material into a pile about the width of the shovel and approximately 10 feet long according to the total amount of material, spreading each shovelful uniformly over the whole length of the pile, beginning alternately from opposite ends. (Fig. 193, C.)

3. Divide the long pile into two equal portions by beginning on one side of the pile, at either end, and take successive shovelfuls, advancing each time by the width of the shovel around the pile, combining the first and every alternate shovelful into a neat cone-shaped pile as in No. 1 and discarding the second and every alternate shovelful (Fig. 193, D and E).

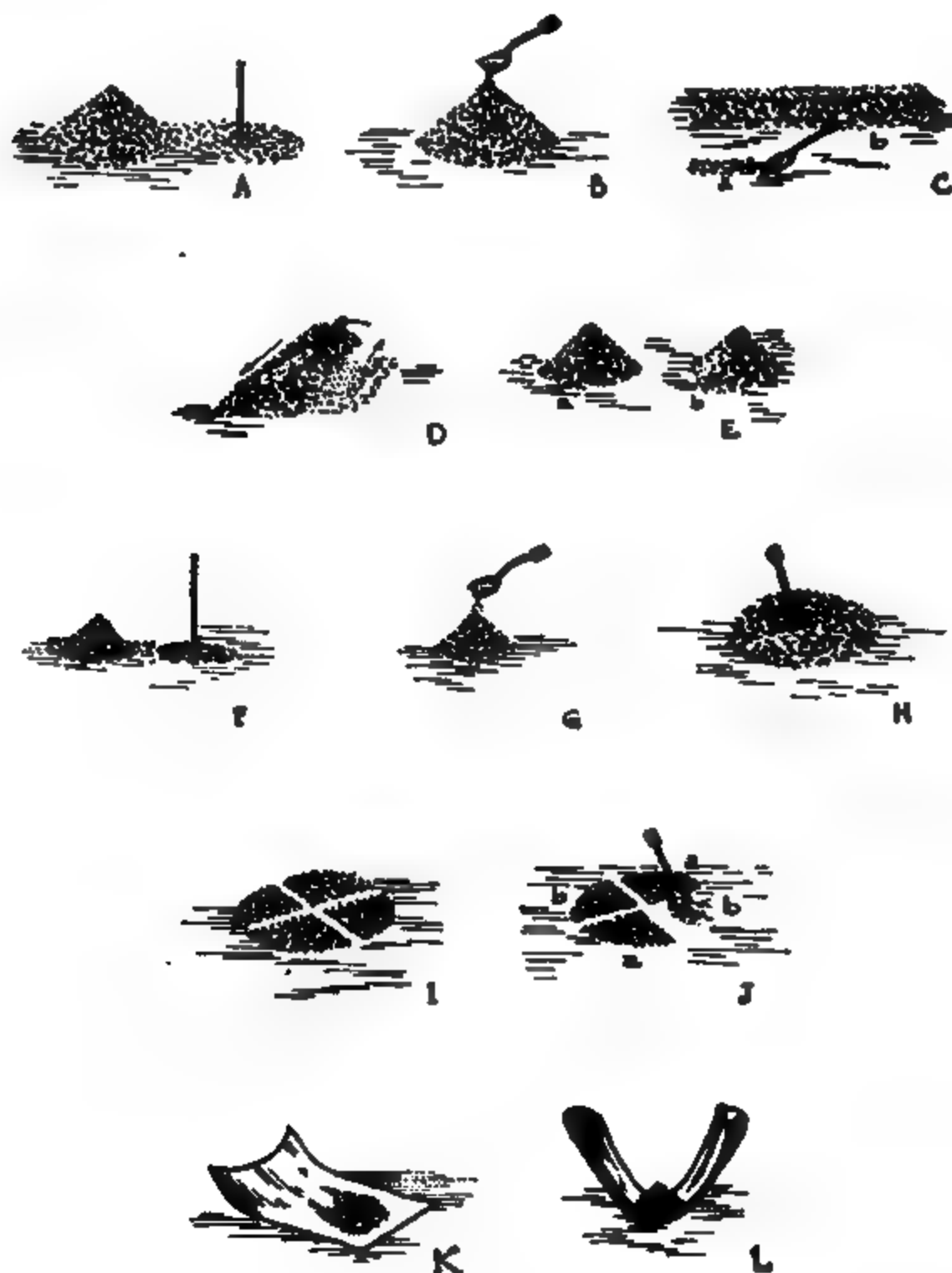


FIG. 193. Method of Sampling Ore.

4. Repeat the above operation on the reserved portion until a portion of about 500 lbs. is obtained.

5. Crush the material until no piece is greater than approximately three-fourths inch in any dimension, and then repeat the above operation (No. 3).

6. Crush the material until no piece is larger than approximately one-half inch in any dimension and then repeat the above operation (No. 3).

7. A portion of about 125 lbs. is now obtained which is further reduced by the "Cone and Quartering Procedure."

### Reduction of Gross Sample (Cone and Quartering)

1. Mix the material amounting to about 125 lbs. by crushing to pass a 4 mm.—5 mesh—sieve and shoveling into a neat cone (Fig. 193, F and G).

2. Flatten the cone by pressing the apex vertically down with the shovel or board so that, when quartered, each quarter will contain the material originally contained therein.

3. Divide the flattened pile into equal quarters by passing a straight edge board vertically twice through center of the pile at right angles, each time drawing half of the pile a few inches to one side (Fig. 193, H and I).

4. Discard two opposite quarters and brush away all fine particles from the exposed surface (Fig. 193, J).

5. Crush the remaining quarters to pass a 2 mm.—10 mesh—sieve. Mix thoroughly by shoveling into a neat cone.

6. Repeat operations No. 3 and 4 or riffle to about 20 pounds.

7. Grind the retained sample to pass a .85 mm.—20 mesh—sieve. Mix the material thoroughly on a clean canvas by raising alternate opposite corners of the canvas, thus rolling the material from side to side one hundred times (Fig. 193, K and L).

8. Treat the sample further as required by the particular material being sampled.

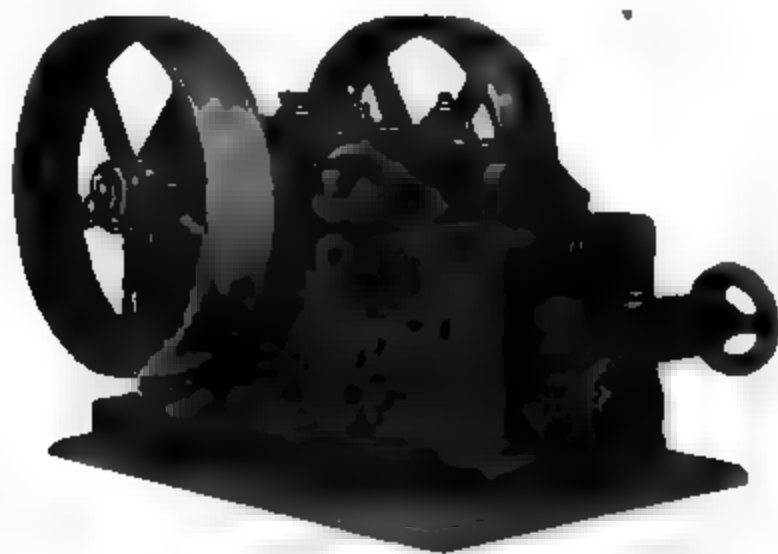


FIG. 194.\* Jaw and Toggle Crusher for Coarse and Medium Fine Grinding.

It is, of course, impossible to reduce hygroscopic or deliquescent gross samples to the laboratory sample according to the above scheme unless they can be dried or otherwise transformed into a stable condition. When it is necessary to reduce such material it should be done rapidly and by hand, under the most favorable atmospheric conditions in regard to humidity, etc. When a large sample is taken for analysis the extent of the reduction of the sample will depend upon the size of the sample taken for analysis.

\* Courtesy of Sturtevant Mill Co.

### Apparatus for Reduction and Preparation of the Sample

Any sampling system which does not properly control the ratio of the size of largest particle to the size of sample can not be depended upon to produce a representative sample. The proper ratio for almost all material will be obtained by following the procedure outlined under the heading "Procedure for Reducing the Gross Sample." This reduction process is greatly facilitated by the use of suitable crushers, grinders, riffle samplers and mixing devices. The following examples of such apparatus are therefore given as an aid to the designing and equipping of the sampling room, the size and capacity of which will be determined by the number, character, and size of the gross samples to be handled.

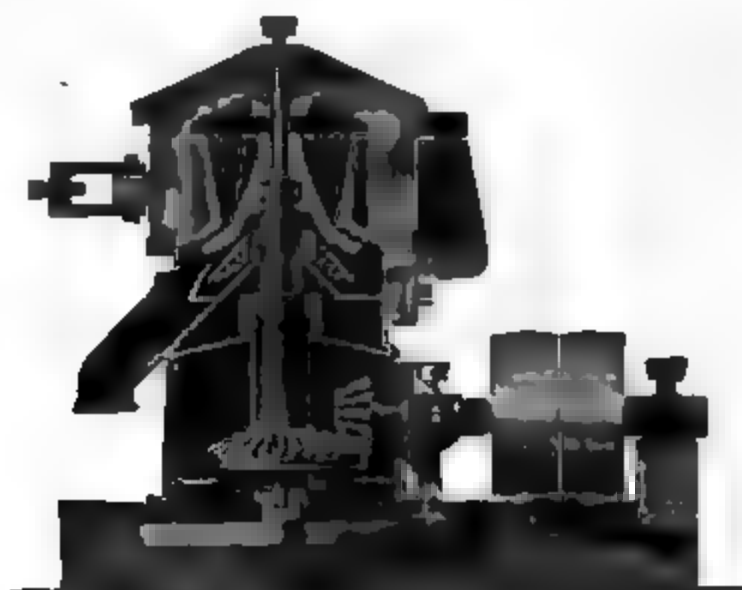


FIG. 195.\* Crusher and Grinder in Cross Section.

**Crushers.**—A jaw and toggle crusher is shown in Fig. 200. This is a satisfactory crusher for coarse, medium and fine crushing and permits a considerable range of adaptability to suit varying conditions and requirements. Simple adjustments allow the capacity to be varied from about 200 pounds per hour for the production of fine material to 700 pounds per hour for coarser material when considering only one of the several sizes of this type of crusher. The parts are readily accessible for cleaning and repairing. By means of this type of crusher it is possible to reduce the material to about 4 mesh.

**Grinders.**—*Grinders* are necessary for reducing the material finer than 4 mesh and may be of the roll, disc or coffee mill type, according to the character of the material.

Roll grinders are especially adapted for brittle material. Figures 196 and 197 illustrate a type of roll grinder which may be readily cleaned and has a capacity of 100 to 1,000 lbs. per hour when producing a reduction to a fineness of 60 mesh and 2 mesh respectively. Disc grinders have a somewhat greater range of adaptability than the roll grinder and will reduce brittle or tough material to a high degree of fineness. The grinding is accomplished between a stationary and a revolving steel or iron disc, the output being small and fine or large and coarse according to the adjustment. Figures 198 and 199 illustrate a satisfactory type of disc grinder.

\* By courtesy of Sturtevant Mill Co.

The coffee mill type of grinder is adaptable to soft or tough materials which have a tendency to stick to the rolls of the roll grinders or to clog the discs of some types of disc grinders. Many kinds of coffee mill type grinders have been developed from which selection can be made according to the character of material under consideration. Figs. 195 and 201 illustrate very good coffee mill types. When reducing material to extreme fineness the ball mill, special small laboratory grinders, the bucking board and mortar and pestle are always applicable for small samples.

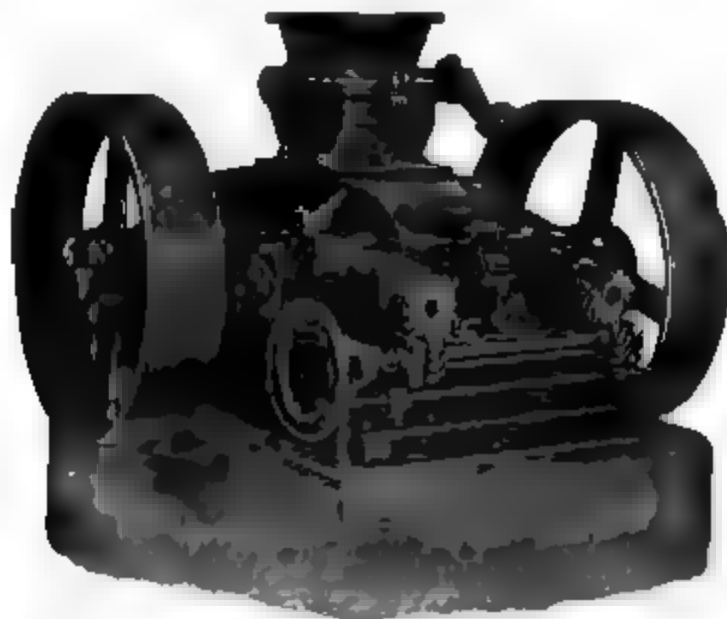


FIG. 196.\* Roll Grinder for Brittle Material.

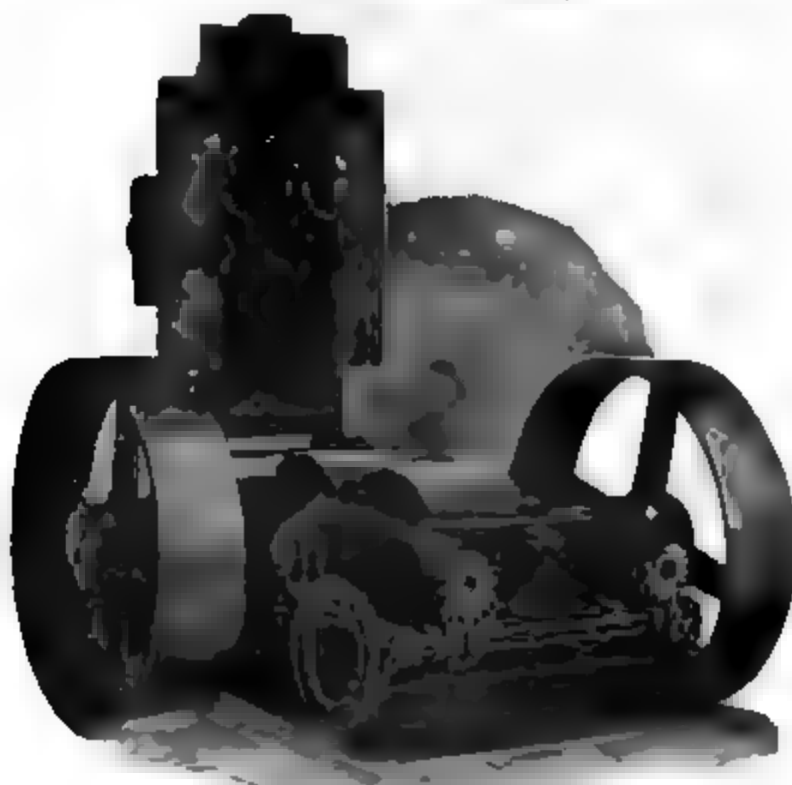


FIG. 197. Roll Grinder with Case Lifted to Show Interior.

Another type of crusher and grinder which has been developed particularly for sampling coal is shown by Fig. 195. This crusher will reduce the material and deliver an accurate ten per cent sample in one operation. By repeating the operation on the aliquot the sample may be further reduced.

For many materials this crusher would serve to entirely reduce the gross sample to the laboratory sample with a very small amount of labor.

\* By courtesy of Sturtevant Mill Co.



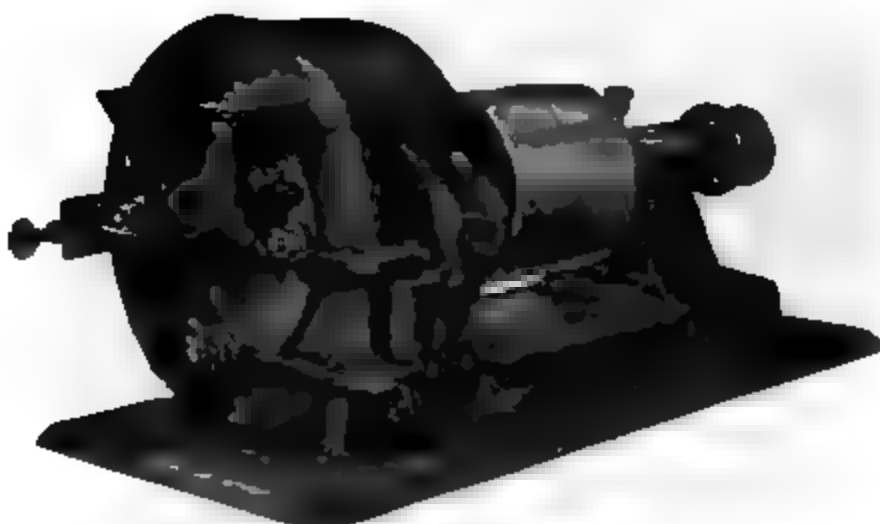


FIG. 198.\* Disc Grinder Ready to Run.

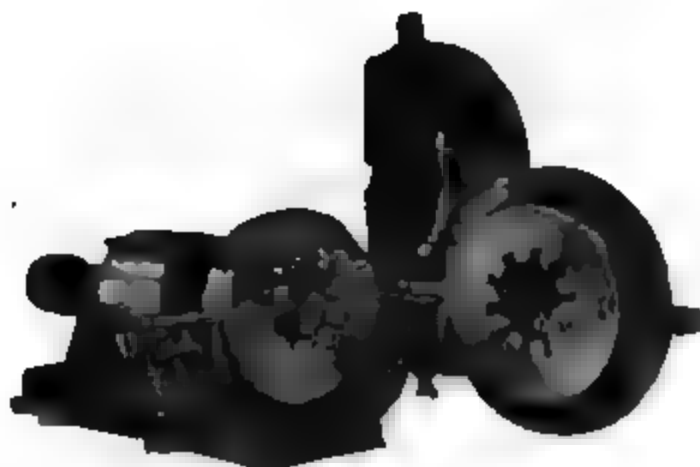


FIG. 199.\* Disc Grinder Open for Cleaning.

\* By courtesy of Sturtevant Mill Co.

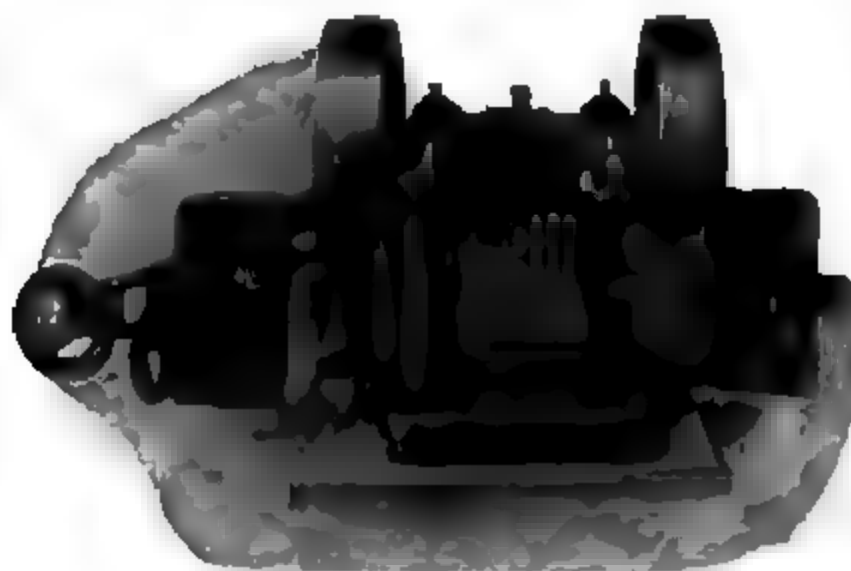


FIG. 200.\* Crusher Open for Cleaning.

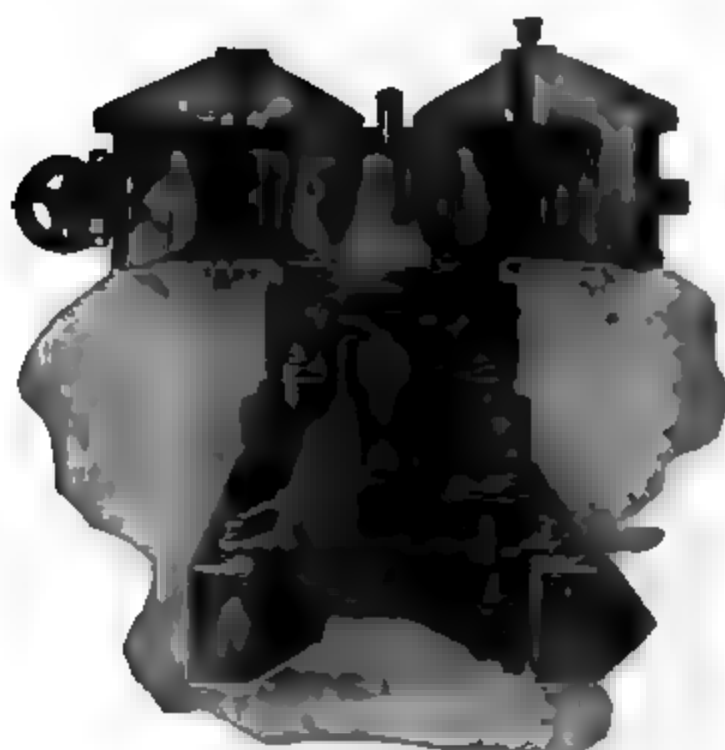


FIG. 201. Combination Crusher and Sampler.

\* By courtesy of Sturtevant Mill Co.

### Mixing and Dividing Samples

Large samples (500 lbs. or more) are usually mixed and divided by the "Long Pile and Alternate Shovel" procedure or (500-100 lbs.) by the "Cone and "Quartering" procedure.

Small samples (less than 100 lbs.) are usually mixed by rolling on a clean canvas, whereby the particles are given a rolling motion in alternately opposite directions, the dividing being done by quartering or, more accurately and rapidly, by passing it through some form of a riffle. A convenient and serviceable type of riffle is illustrated by Fig. 202. Another and more simple type is shown by Fig. 203.

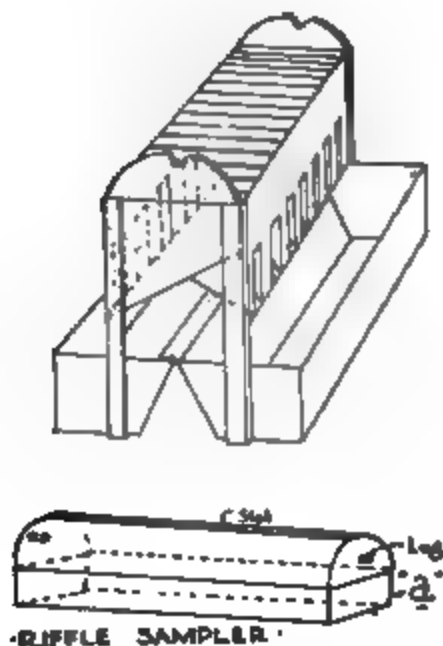


FIG. 202.



FIG. 203.

FIG. 202. Riffle Sampler. "a," cover to fit tightly over one of the boxes with slot in rounded tops—also fitted with two lugs which fit in ends of riffle and help to rock evenly.

FIG. 203. The cut shows the apron of the cylinder of this machine open for receiving the sample. After the sample is poured in, the apron's position is shifted, *a* being moved to *a'*. The cylinder is then revolved counterclockwise. The closed sides of the riffles plow through and thoroughly mix the sample, and no sample can be discharged through the riffle while the cylinder is revolving in this direction if the level of the sample is below the axis of the cylinder. After the sample has been mixed the cylinder is rotated one turn clockwise; the sample in the cylinder is then cut by the planes of the riffle and half of it is discharged into the receiving tray. The sample remaining is again mixed by revolving the cylinder counterclockwise. By alternately changing the direction, the sample is alternately mixed and halved until twice the size of sample required remains in the cylinder. The tray is then emptied of the discarded material, and the sample remaining, mixed and halved, and the sample caught in the tray is bottled and becomes the official sample, while the sample remaining in the cylinder is bottled and held as the reserve sample. The interior of the machine is easy of access and should be brushed clean after each sampling operation.

### The Use of Standard Sieves

This section is based upon the specifications issued by the U. S. Bureau of Standards (1912) and adopted by the Amer. Inst. of Mining Engineers (1917).

The essential quantity in the definition of a sieve of a particular size is, primarily, the size of the openings through which the particles to be sifted are to pass.

A series of sieves of different sizes should have the openings vary uniformly, according to the size of the particles desired to separate. Inasmuch as most of the grinding of substances to fine particles is chiefly with the object of increasing the surface upon which some chemical action is to take place, the opening of such a series of sieves should vary in such a way that the square or fourth powers of the width of the openings shall form a geometrical series.

Designation of Sieve, Metric System	Customary Usage	Opening		Number of Mesh per Linear		Diameter of Wire	
		Mm.	Inch	Centimeter	Inch	Mm.	Inch
128	mm.	128.0	5.04			9.5	0.375
90.5	"	90.5	3.56			9.5	0.375
64	"	64.0	2.52			6.4	0.25
45.3	"	45.3	1.78			5.26	0.207
32.0	"	32.0	1.28			4.85	0.192
22.6	"	22.6	0.891			4.11	0.162
16.0	"	16.0	0.630			3.00	0.120
11.3	"	11.3	0.445			2.67	0.105
8.0	"	8.0	0.315	1.0	2.54	2.00	0.079
5.66	"	5.66	0.223	1.4	3.56	1.48	0.058
4.00	"	4.00	0.157	2.0	5.10	1.00	0.039
2.83	"	2.83	0.111	2.75	7.00	0.81	0.032
2.00	"	2.00	0.079	3.9	9.9	0.56	0.022
1.41	"	1.41	0.055	5.0	12.7	0.59	0.0232
1.00	"	1.00	0.0394	7.0	17.8	0.43	0.0169
.85	"	0.85	0.0335	8.0	20.3	0.40	0.0157
.71	"	0.71	0.0280	9.0	22.9	0.40	0.0157
.59	"	0.59	0.0232	10.0	25.4	0.41	0.0161
.5	"	0.50	0.0197	12.0	30.5	0.33	0.0130
.42	"	0.42	0.0165	14.0	35.6	0.29	0.0114
.36	"	0.36	0.0142	16.0	40.6	0.26	0.0102
.29	"	0.29	0.0114	20.0	50.8	0.21	0.0083
.25	"	0.25	0.0098	23.0	58.4	0.185	0.0073
.21	"	0.21	0.0083	27.0	68.6	0.16	0.0063
.17	"	0.17	0.0067	31.0	78.7	0.15	0.0059
.14	"	0.14	0.0055	36.0	91.4	0.116	0.0046
.125	"	0.125	0.0049	47.0	119.4	0.095	0.0038
.105	"	0.105	0.0041	59.0	149.9	0.084	0.0033
.088	"	0.088	0.0035	67.0	170.2	0.061	0.0024
.074	"	0.074	0.0029	79.0	200.7	0.053	0.0021
.062	"	0.062	0.0024	98.0	248.9	0.040	0.0016
.052	"	0.052	0.0021	110.0	279.4	0.039	0.0015
.044	"	0.044	0.0017	127.0	323.0	0.035	0.0014

While the sampling process does not require extremely accurate sieves it is advisable to use those which conform approximately to a standard specification. Consequently whenever reference is made to a sieve it will be understood to comply with the following specifications, which have been adopted by a conference of representatives of various scientific and technical societies, government bureaus, and private firms, held at the U. S. Bureau of Standards.

This sieve scale is essentially metric. The sieve having an opening of 1 mm. is the basic one and the sieves above and below this in the series are related to it by using in general the square root of 2 (1.4142), or the fourth root of 2 (1.1892), as the ratio of the width of one opening to the next smaller opening. The first ratio is used for openings between 1 mm. and 128 mm. while

the fourth root of 2, is used as the ratio for openings below 1 mm. to give more sieves in that part of the scale.

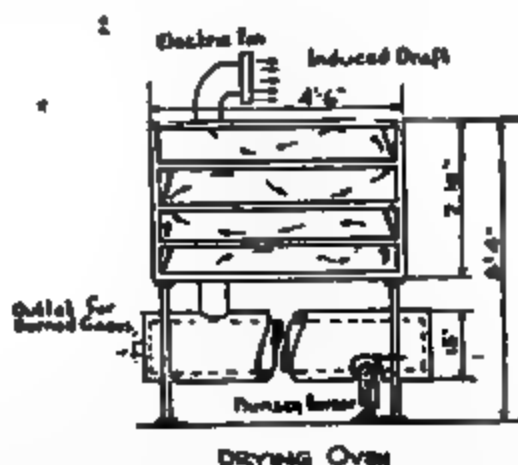


FIG. 204. Dryer for Coarse Samples. The outlet for air at the top may be connected with a chimney or any other device which will furnish a suitable draft. The sample is spread on tared pans, weighed, and dried at  $10^{\circ}$  to  $15^{\circ}$  C. above room temperature, and weighed again. The drying should be continued until the loss in weight is not more than 0.1 per cent per hour.

### Containers for Shipment to Laboratory

Samples in which the moisture content is important should always be collected and shipped in moisture-tight containers. A galvanized iron or tin can with a screw top which is sealed with a rubber gasket and adhesive tape is best adapted to this purpose. Glass fruit-jars sealed with rubber gaskets may be used, but require very careful packing to avoid breakage in transit. Samples in which the moisture content is of no importance need no special protection from loss of moisture.

### Drying Ovens for Moisture Determination

Samples may be dried by means of a forced draft of air at a slightly elevated temperature, or by heating at  $100$ – $110^{\circ}$  C. in a well-ventilated oven until a constant weight is obtained. The former procedure is particularly adapted to material which has a tendency to undergo undesirable chemical or physical changes upon prolonged heating at elevated temperatures or for rapidly removing extraneous moisture preparatory to grinding. The latter procedure is usually employed for quantitative determinations on small finely ground samples. In either case a good system of ventilation and a definite uniform temperature are the chief considerations.

Figure 204 illustrates an oven for drying large samples by means of a current of heated air. Figs. 205 and 206 show a type of oven with a good ventilating system. Fig. 207 shows another type of oven, while 208 illustrates a vacuum drying oven which may be necessary for special work.



FIG. 205.

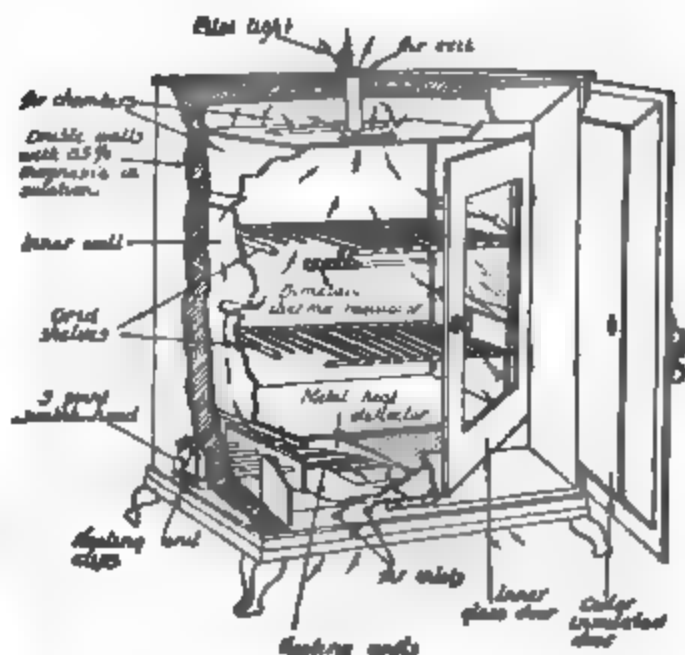


FIG. 206.

FIGS. 205 AND 206. Drying oven, triple walled, with a layer of air entirely surrounding the inner chamber, the temperature of this layer being practically the same as that of the air in the chamber. This approaches an adiabatic construction which has been approved by the Bureau of Standards as the best type of design for calorimeters and other constant temperature devices. By this construction together with a heavy outer insulation, heat exchanges between the inner chamber and the room outside are practically entirely prevented, and as a result a uniformity of temperature is secured in the heated space. The drying chamber should be entirely shielded from direct radiation from the heating units, and into every part of which heat should be carried by convection currents.



FIG. 207.\*

High Temperature Ovens, for operation from room temperature to 260° C.

\* By courtesy of Arthur Thomas Co.

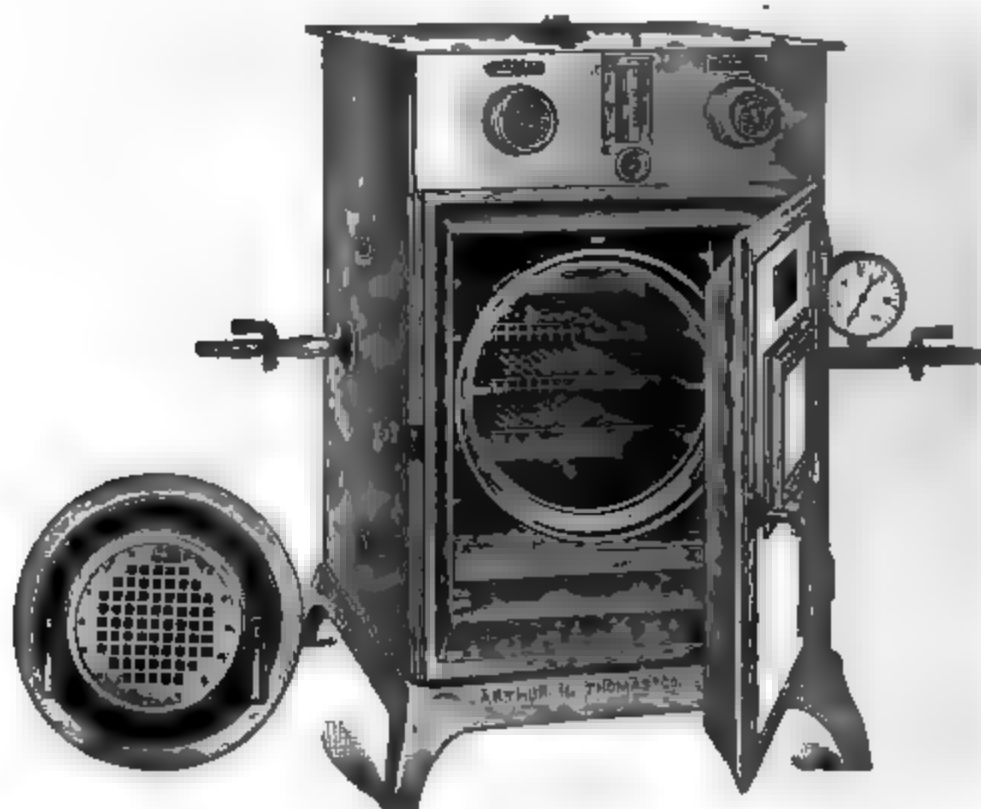


FIG. 208.\* Vacuum oven. Supplied with a vacuum chamber which may be easily removed, permitting the oven proper to be used as a regular drying oven when the vacuum feature is not desired. Moisture test of flour can be made in five hours at 75 C., while in an ordinary oven at 100 C. from ten to twelve hours are required. The same condition apply for organic tests in general, i.e., for fertilizers where the tests must be made at the lowest possible temperature to avoid driving off nitrogen compounds; for powder where there is great danger of igniting the sample; for milk where there is great danger of charring; for operations involving essential oils, etc.

When tests are to be conducted in an atmosphere of hydrogen, nitrogen, carbon dioxide or other gas, it is only necessary to pass a current of the desired gas through the vacuum chamber.

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\* By courtesy of Central Scientific Co.

## GENERAL OUTLINE FOR SAMPLING LIQUIDS

In general, a uniform and representative sample of liquid material is a feasible possibility because of the usual absence of segregated constituents, the ease with which the separate components may be intimately mixed, and the degree of comminution to which a liquid may be subjected without producing a separation of the individual components.

When the liquid is thin, non-viscous, and does not contain immiscible constituents, a homogeneous condition usually exists, and a sample from any part of the bulk is sufficiently representative of the whole. When viscous or immiscible materials are present, a heterogeneous condition usually exists and extreme care must be exercised to obtain a thoroughly representative sample. The proper selection of a representative sample of a liquid therefore, involves a consideration of the physical laws of liquids, their chemical activity, the miscibility of all components, and the interference of any insoluble materials carried by the liquid.

The sampling of liquids is divided into the three following classes; sampling liquids in quiescent state, sampling liquids in motion, sampling special liquors, *e. g.*, immiscible liquids, volatile liquids, liquids carrying sediment, etc.

## Sampling Liquids in Quiescent State

All liquids not in motion may be sampled by obtaining portions at specified points from the top to the bottom of the liquid by means of a suitable sampling apparatus.

1. From Storage Tanks, Tank Cars, Boats, Evaporating Kettles, Vats, Crystallizers, Mixers, Settlers, Etc.

(a). If the liquid has been thoroughly agitated or is known to be reasonably uniform in composition, transfer several portions to a container by means of a suitable dipper, the several dippings being taken promiscuously throughout the mass of liquor.

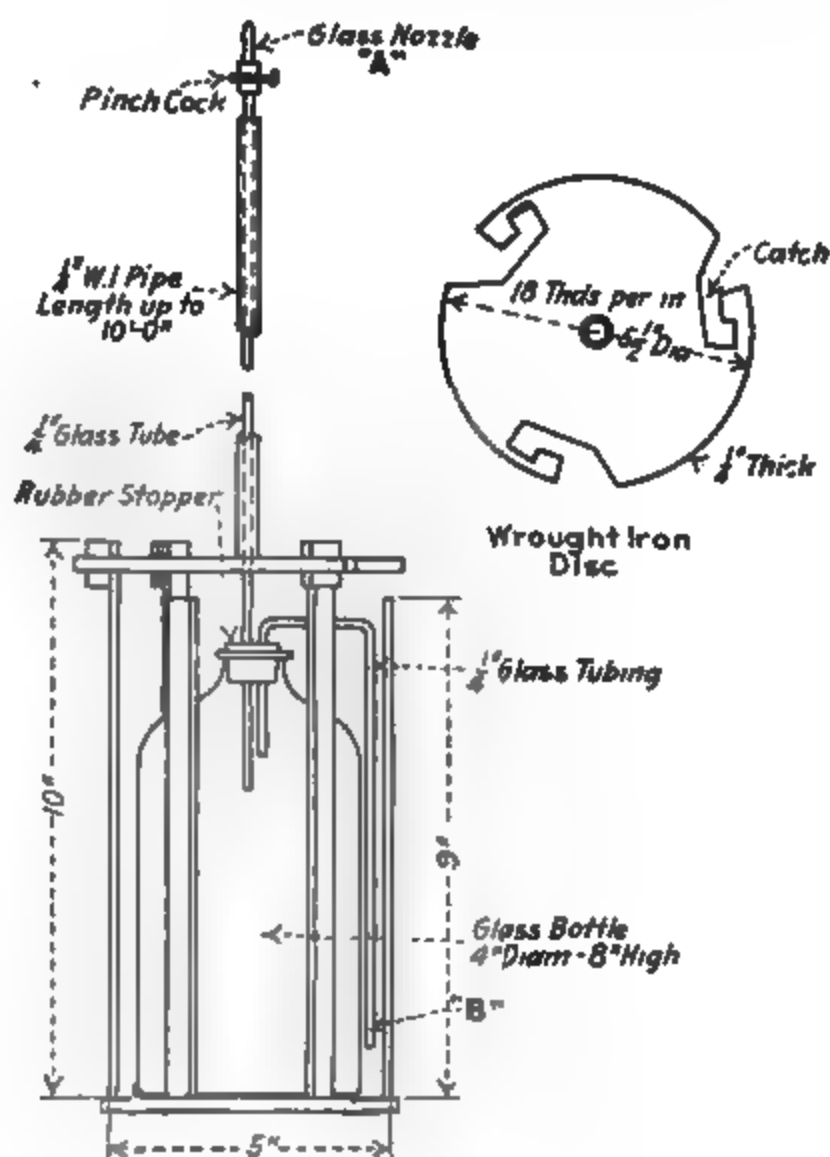


FIG. 203. Sampling liquids apparatus.



(b). If the character and condition of the liquid is such as to permit the formation of zones of different composition, obtain samples by means of a suitable apparatus as shown by Fig. 209, whereby proper proportions of the liquid are taken at every point from the top to the bottom. Combine these samples for the gross sample and, after thoroughly mixing, bottle the required samples (Fig. 209). By slowly lowering the sampling bottle into the liquid with the outlet (A) open, a portion of the liquid from every point passes through (B) into the bottle, whereas if outlet (A) is kept closed until the desired depth is reached, the entire sample may be taken at any desired point.

Lead, wood, or any other material which is resistant to the liquid may be substituted for the iron parts of this device, according to the character of the liquid being sampled. Under some conditions it will be necessary to substitute a ground glass stopper for the rubber one. Openings of different sizes can be attached at (A) to govern the rate at which the sample will flow into the bottle.

(c). Take a sample from the upper, middle, and lower levels of the liquid by means of a sampling device similar to that shown by Fig. 209, by keeping the outlet tube A closed until the container has been lowered to the desired depth.

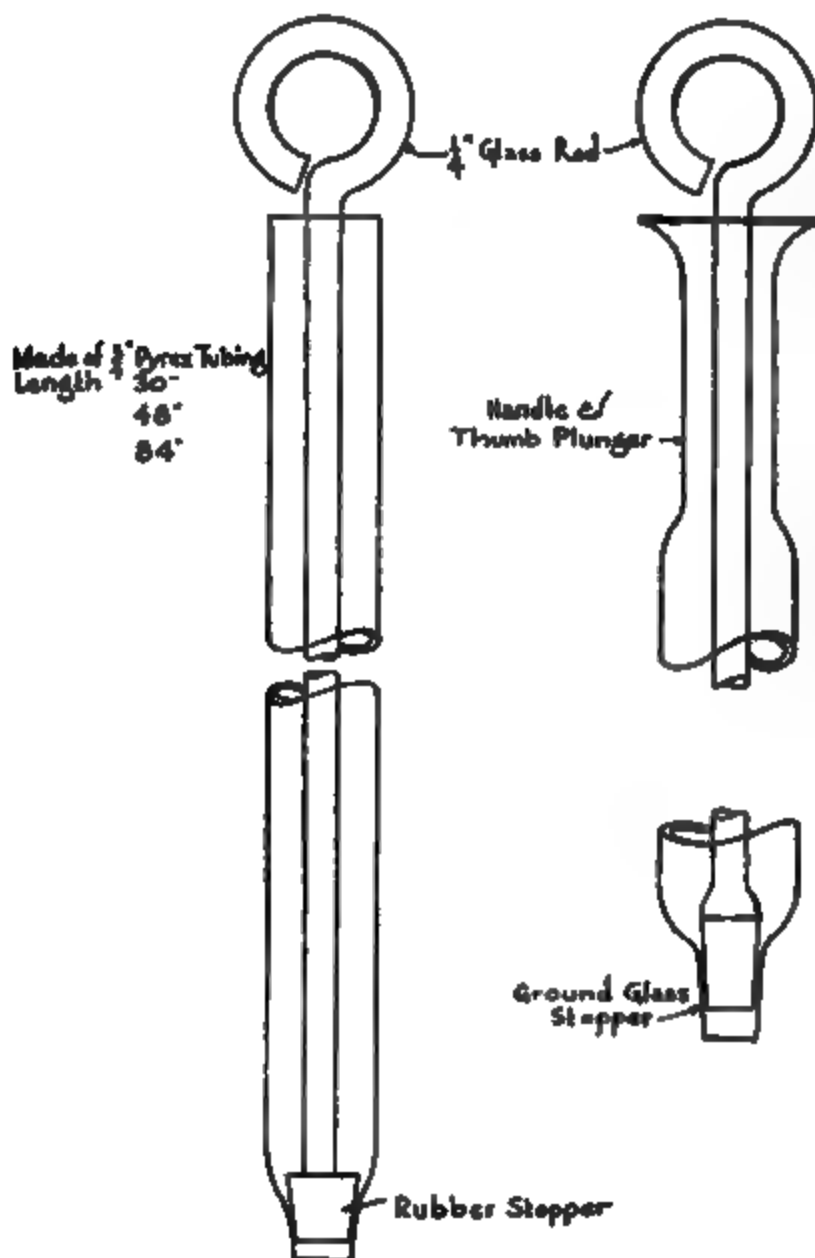


Fig. 210. Sampling liquids apparatus.

## 2. From Drums, Carboys, Barrels, Etc.

(a) By means of a thief (Fig. 210) take proportional fractions from each container. Combine and mix these increments for the composite gross sample. Bottle the amount required for the sample. If the contents of the container are such as to preclude thorough mixing or if the material has a tendency to form strata of varying compositions, the open thief should be lowered into the liquid at such a rate as to keep the levels of liquid inside and outside of the thief very nearly equal, in order to include portions at all points from the top to the bottom of the liquid.

### Sampling Liquids in Motion

#### 3. From a Pipe or Conduit Carrying a Continuous Full Flow under a Constant or Varying Head

(a) A continuous or intermittent sample may be taken by inserting a small pipe into the line on the discharge side of the pump or propelling force of the flow. This sampling tube should extend one-half of the distance to the center of the flow, with the inner open end turned at an angle of  $90^\circ$  and facing the flow of the liquid. The sampling tube may be supplied with a stopcock in order to regulate the flow into a receiver. The amount drawn during the period of taking a continuous sample constitutes the gross sample. In this instance the stopcock should be adjusted at the beginning of the sampling period, to give the desired flow and no readjustment made during the sampling period. Intermittent samples may be taken by opening the stopcock for a definite period of time at definite intervals. The combined intermittent samples then constitute the gross sample.

#### 4. From a Pipe or Conduit Carrying a Varying Fraction of Flow

(a) By means of a sampling weir similar to the apparatus shown by figure 212, a definite fraction of varying flow can be collected over a required period

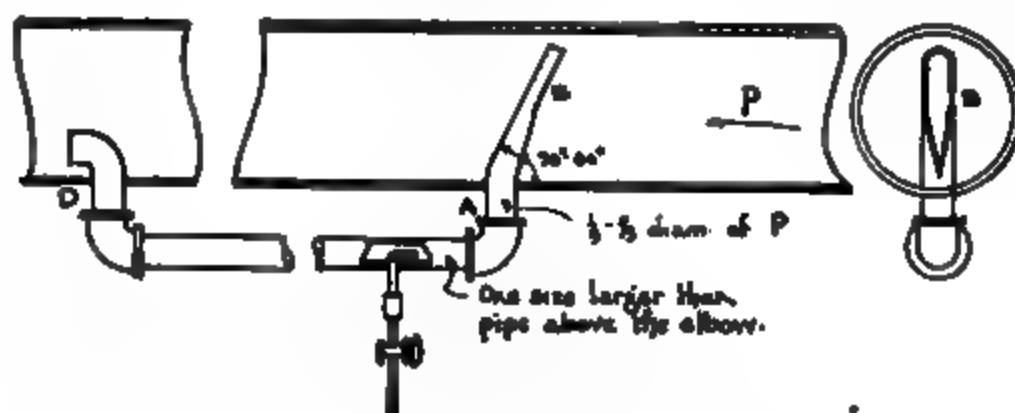


FIG. 211. Apparatus for Sampling Liquids in Motion.

of time. This gross sample may be mixed and a portion taken for the final sample or by connecting two or more of the above devices in series; a small representative sample may be collected automatically, *e.g.*, if one million gallons of liquid per day are passing through a pipe or conduit line at an irregular rate, it could be sampled by conducting the stream to a series of four sampling weirs, each of which separates 5% or  $1/20$  of the flow. A final six gallon sample would then represent the entire million gallons. The size of each weir should be such as to give a suitable overflow and the apron over which the flow passes for division should be fixed in a horizontal position.

(b) By means of the arrangement illustrated by Fig. 211, an approximate sample ratio can be continuously diverted from a non-uniform flow. This device consists of a pipe A, inserted into the flowing stream at an angle of  $70-80^\circ$  provided with an opening B facing the flow and extending to the top of pipe P. This opening B is constructed as shown in the cut (Fig. 211), the width above the center of pipe P being equal to the diameter of pipe A, then

tapering from the center to the bottom of the pipe *P*. As the flow passes pipe *A*, an approximately constant sample ratio is diverted through pipe *A* and is sampled by a small pipe *C*, the opening of which faces the flow at a point

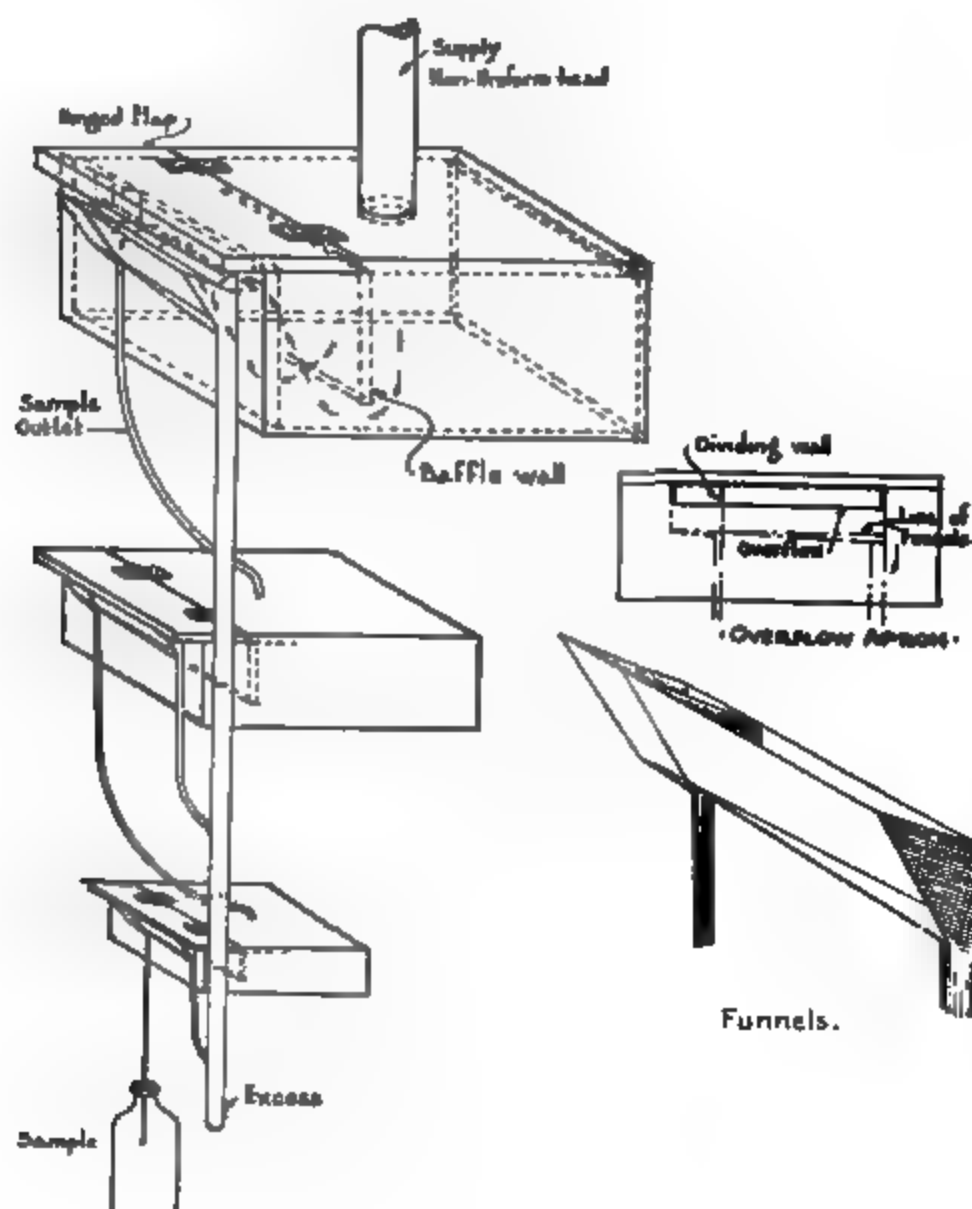


FIG. 212. Apparatus for Sampling Liquids.

halfway between the center and bottom of pipe *A*. Pipe *C* is fitted with a stopcock whereby the amount of the sample flow through *C* may be regulated. Pipe *A* reenters pipe *P* at some point which will give sufficient positive flow-head through *A*. While this arrangement will not necessarily produce an

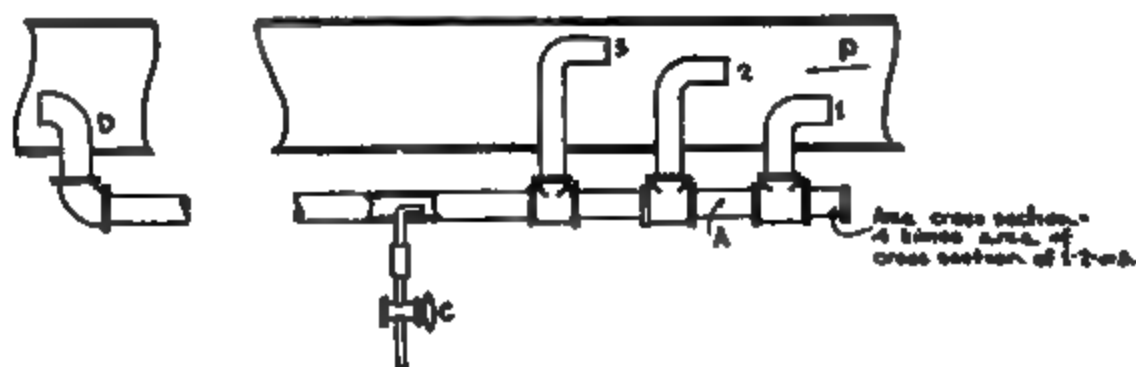


FIG. 213. Apparatus for Sampling Liquids in Motion.

accurate sample ratio, an increased flow through *P* will increase the flow-head through *A* and consequently increase the amount of sample withdrawn at *C* and an approximately relative sample ratio will be maintained with one regulation of stopcock *C*.

(c) With large pipes and large flows, the above arrangement may be modified as shown by Fig. 213. Three pipes, 1, 2, and 3, bent at 90° angles with openings facing the flow at different levels are inserted in pipe *P* and connected to a common pipe *A*. The flow through *A* is then sampled by a pipe *C* as described above. An approximately relative sample ratio is thus maintained with one regulation of stopcock *C*.

### Sampling Special Liquids

#### 5. Liquids Containing Insoluble Matter in Suspension

(a) When the sediment remains in reasonably uniform suspension during the period required for taking the sample, the liquid is thoroughly mixed and the sample obtained by one of the foregoing procedures.

(b) When the sediment settles rapidly or is impossible of uniform distribution it is necessary to take special precautions to secure the components of the sample in the proper proportion. This can be accomplished with a fair degree of accuracy by mixing the liquid thoroughly and then rapidly taking a complete column of the liquid by means of the special thief or device shown by Fig. 209 or 210. By repeating this operation a number of times, a fairly representative sample will be obtained. Another procedure of possible application under certain conditions would be to take several portions at as many uniformly distributed points from the top to the bottom by means of the thief Fig. 209 or 210. These portions are then combined and mixed for the gross sample.

(c) To accurately sample a liquid containing insoluble matter, it is necessary to filter the entire liquid, weigh the insoluble material and filtrate separately and then take separate samples of the sediment and liquid, recording the ratio of sediment to liquid for use in the final evaluation of the original material. This, however, is impracticable except in such instances wherein the size of sample allows of economical handling in the manner described.

#### 6. Liquids Composed of Immiscible Layers

The most practical and accurate procedure in this case is to effect a separation of the layers and combine portions of each layer in the proper ratios. If this is impossible, the material may be transferred to a container of uniform cross section, the depth of each layer measured, and then the proper portion taken from each layer, for a composite sample, by means of a sampling thief similar to those shown in Fig. 209 and 210.

#### 7. Liquids Containing Crystals Due to Supersaturation

Frequently conditions are such that a portion of the liquid or certain constituents thereof have crystallized in the container. Oleum and acetic acid are common examples of this class. When practical the material should be warmed sufficiently to dissolve completely or melt the crystals before sampling by one of the foregoing procedures. Otherwise, if the crystals are small and remain in suspension the mass should be sampled as a liquid containing insoluble matter in suspension.

### 8. Volatile Liquids

(a) Volatile liquids are best sampled from a continuous flow while the liquid is being discharged or by means of a siphon from containers. If the liquid is uniform in composition or can be made so by agitation in some manner, a portion may be run to the bottom of the sampling bottle until the bottle overflows through another tube from the top into another bottle or to the waste pipe, to such an extent as to leave a liquid in the first bottle containing the maximum amount of the volatile constituent (see Fig. 214). The sample bottle should then be quickly stoppered and sealed for transportation to the laboratory.

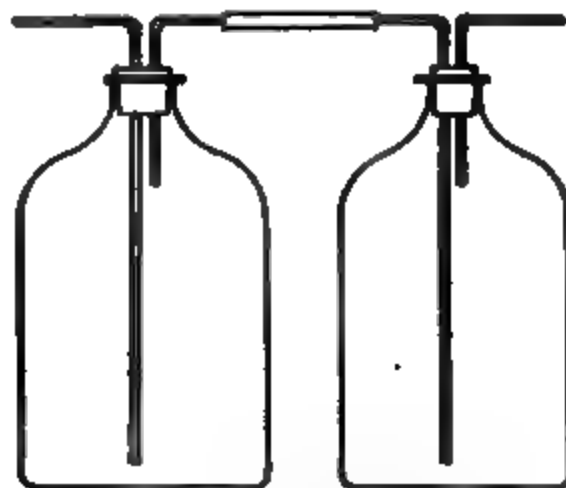


FIG. 214. Apparatus for Sampling Liquids.

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## GENERAL OUTLINE FOR SAMPLING GASES

The proper sampling of gases often presents greater difficulties than the analysis. This is particularly true when it is desirable to obtain a representative sample of a gas during a considerable period of time as it passes through a pipe or flue from the source of production. Gases travel through straight pipes and conduits in an irregular succession of waves with a spiral motion, the maximum velocity being at the center of the pipe and the minimum near the walls. The motion of these waves and point of maximum velocity is altered in a varying degree by every bend and obstruction throughout the line of travel. Where gases are encountered which are subject to temperature changes either above or below normal, this factor will also considerably interfere with proper sampling. The temperature of gases will vary throughout the cross-section of the pipe, usually being hottest at points of maximum velocity and coldest next to the walls and in dead pockets. Theoretically if it were possible to discharge the total gas to be sampled into a large holder and provide time for it to thoroughly diffuse, it would then be in the most advantageous condition whereby a true and representative sample could be obtained by simply withdrawing a portion. Unfortunately this is not often the condition under which gases are to be sampled, being usually sampled from a flow possessing varying velocity, temperature, and composition. Under such conditions it is practically impossible to determine a point of approximate average velocity, temperature or composition from which a representative instantaneous sample can be drawn.

Consequently it becomes necessary to collect a sample over an extended period whereby the number of series of gas waves sampled is such that there is a high probability that a true and representative sample will be obtained. Under some conditions, useful and more definite data regarding composition and gas-flow is obtained by taking frequent "grab" samples. It is, therefore, quite evident that the subject of gas sampling naturally divides itself into two phases for consideration that of continuous sampling and "grab," or instantaneous, sampling.

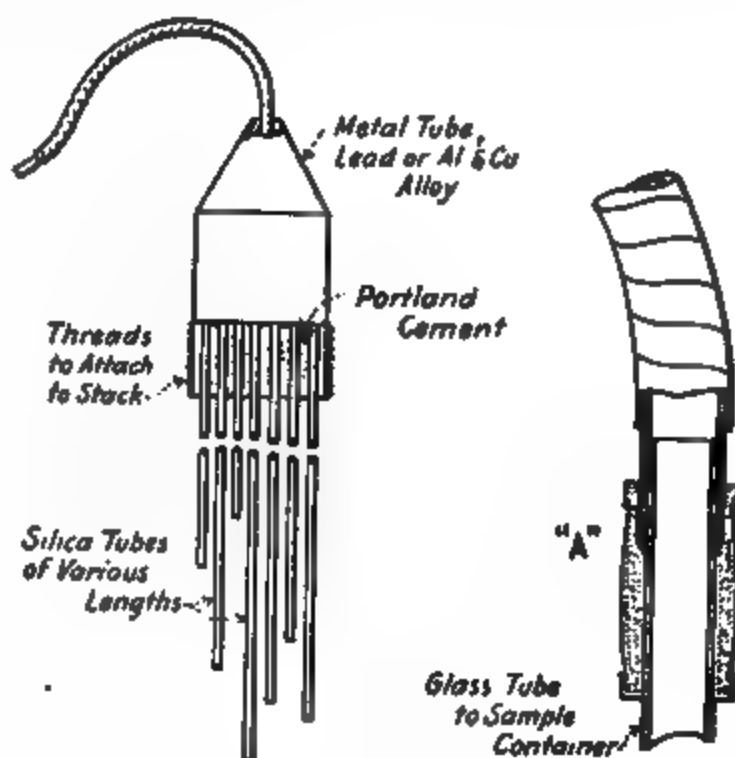


FIG. 215. Apparatus for Sampling Gas.

## 1. General Considerations and Apparatus

(a) **Sampling-tube for Drawing Samples from Gases Flowing through Pipes.**—Without discussing the merits of the various forms of sampling tubes such as the single-opening tube, and the various types of perforated tubes all of which are more or less useful under certain conditions, the multiple type originated by A. H. White—"Gas and Fuel Analysis"—is apparently best adapted for securing uniform samples (see Fig. 215). This tube should be inserted so that the longest tube reaches the center of the flowing gas.

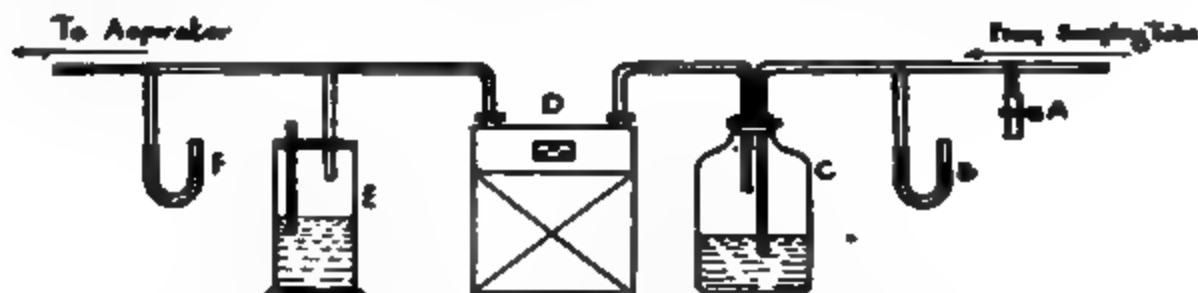


FIG. 216. Apparatus for Sampling Gas.

(b) **Collecting a Representative Continuous Sample.**—In order that the sample should be truly representative of the total gas flowing during a definite period, it is necessary to constantly draw a definite proportion of the gas. Great elaboration of apparatus and equipment would be necessary if the rate of drawing the sample were adjusted to vary directly with the velocity of the gas, in which case the sample would accurately represent the gas. The most practical approach to this ideal condition would be to take the continuous sample under a constant pressure, whereby the rate of sampling will vary directly with the pressure of the gas being sampled.

Figure 216 illustrates a common form of apparatus whereby a stream of gas at constant pressure is drawn from a gas line. This apparatus consists of a pressure-gage *B* to indicate any obstruction of the sampling tubes, a bubbling-bottle *C* to give a visual control of the rate of the stream, a gas-meter *D* which may be omitted if not needed, a pressure control, *E* and a pressure gage *F* on the line to the aspirator. When aspiration is necessary the pressure at the sampling-tube as shown by gage *B* should be only a few tenths-of-an-inch of water. This may be regulated by the depth to which the tube is immersed in the water of the regulator *E*. When the gas is under pressure, the aspirator and *E* and *F* become unnecessary.

(c) **The Design of Apparatus.**—The design of apparatus—and the sampling procedures—must take into account the solubility and chemical activity of the gas. Saturated magnesium chloride solution, glycerine and water mixtures, and various oils have been used with varying success in overcoming the solubility of gases in the solutions over which they are collected. Further

investigations along these lines for specific gases will probably make possible the use of other liquids than mercury for gases having high solubility factors. The corrosive character of the individual gases will determine the type of containers, etc., which may be used.

### 2. Taking a "Grab" Sample

(a) For a "grab," or instantaneous, sample the ordinary two-bottle aspirator may be used (see Fig. 217) using care not to draw the sample so fast as to produce a reduced pressure at gage *B* (Fig. 216).

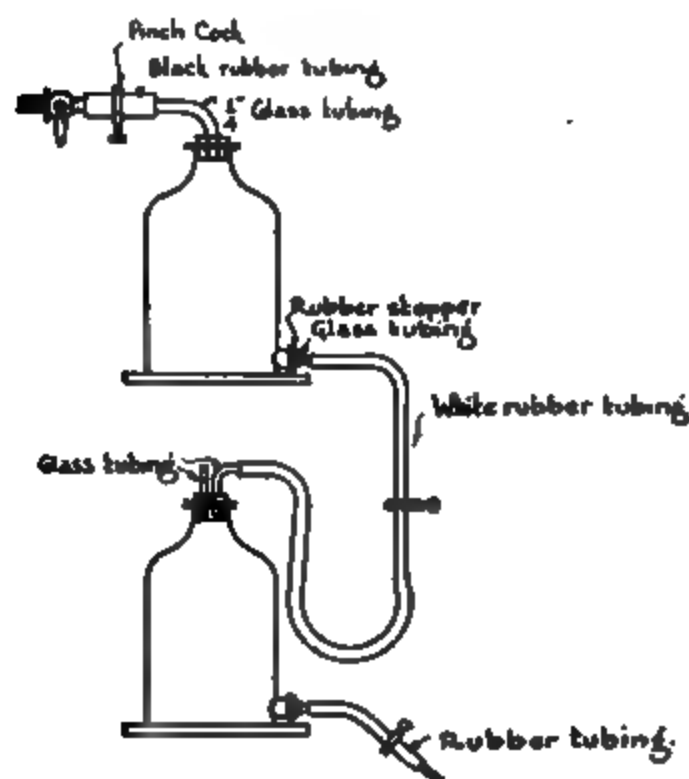


FIG. 217. Apparatus for Sampling Gas.

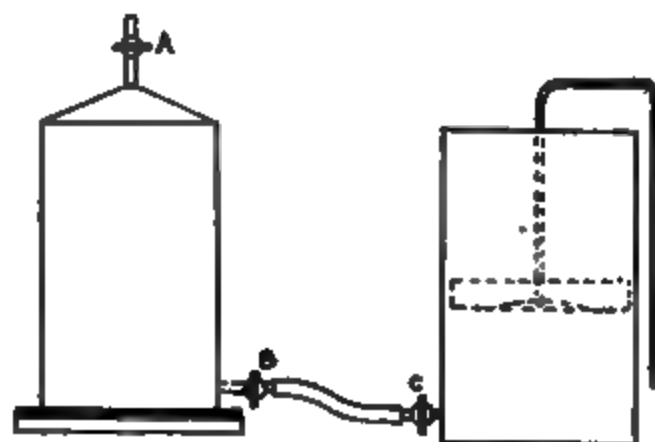


FIG. 218. Apparatus for Sampling Gas.

### 3. Taking a Continuous Sample

(a) For continuous sampling the apparatus illustrated by Fig. 218 will be found convenient.

This apparatus consists of two large galvanized metal tanks, one in the form of an aspirating-bottle in which the sample is taken, and the other, slightly larger, which acts as a reservoir. A sample of gas taken under constant pressure and at a uniform rate over any specified period of time, which may be varied at will, is obtained by filling the tanks with water, oil or other liquids according to the character of the gas, until the level reaches the top of the aspirating-tank. A syphon acts as the outlet and a uniform rate, if the pressure of the gas is constant, is obtained by attaching it to a wooden float. The speed of outflow may be regulated by the length of the syphon and the opening or size of the outlet-nozzle.

By arresting the downward movement of the float and syphon by means of a shoulder or suitable device, a small amount of water remains in the aspirator; this acts as a seal and automatically discontinues the intake of gas. By closing the stopcocks *A* and *B* the operation is completed.



These tanks may be constructed to crate, in compact form for transportation, a 20-liter glass aspirating-bottle, as shown in Fig. 219.

This bottle is to be used when the gas to be sampled would attack the metal aspirating-tank. If a layer of some non-absorbing oil is placed on the surface of the water the original composition of the gas is unaffected.

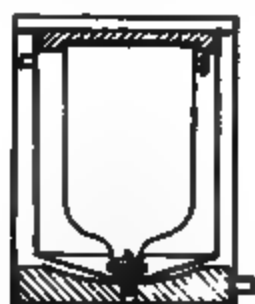


FIG. 219. Apparatus for Sampling Gas.

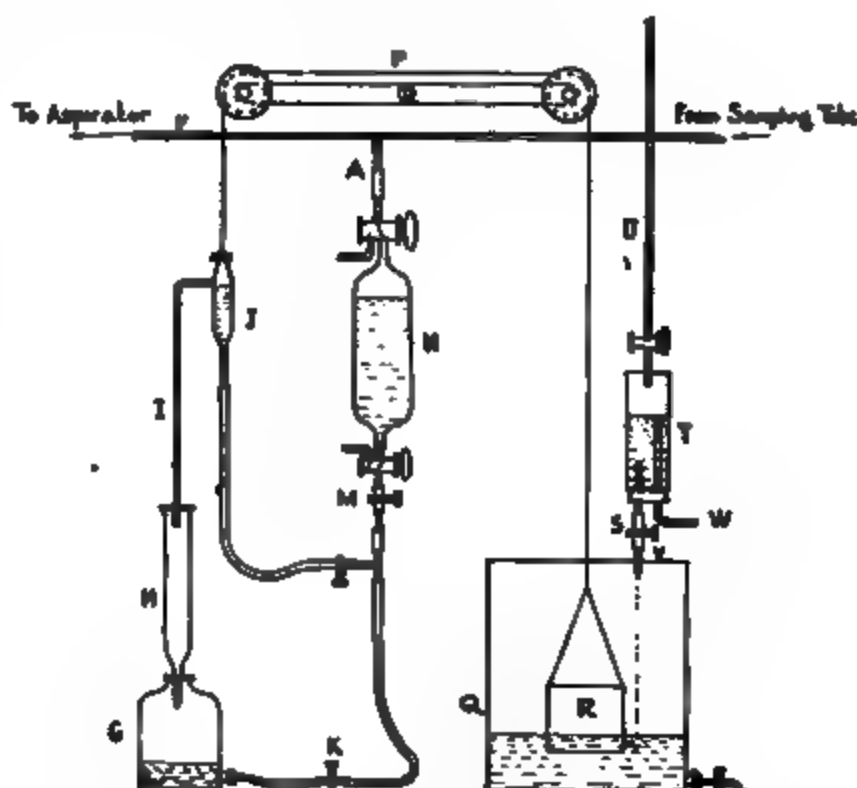


FIG. 220. Apparatus for Sampling Gas.

(b) When mercury must be used because of the solubility of the gas in water, an apparatus similar to that illustrated by Fig. 220, originated by Thomas Gray, *J. Soc. Chem. Ind.*, 32, 1092, will be found convenient.

"It consists essentially of an ordinary gas-sampling tube *N*, attached to a reservoir *J*, which is counterpoised by a vessel *R* floating in a tank *Q*, the float being connected with *J* by means of a cord which passes over the pulleys *P*.

"The float *R* may be a tinned-iron vessel or glass bottle containing the necessary quantity of water or lead shot to establish the balance. The height of the tank *Q* must be greater than the length of the sampling-tube *N*, the overflow-tube *I* should be slightly longer than *N*, and the length of the wider tube *H*, which merely serves to prevent loss of mercury by splashing, should slightly exceed that of *I*.

"The jet *V*, under pressure which may be regulated by adjustment of the overflow *W*, through which the excess of water from *U* escapes to the waste, delivers sufficient water during the specified period to raise the level in the tank to a height equal to the length of the sampling-tube.

"As the water-level rises, the reservoir *J* is steadily lowered, drawing the gas uniformly into the sampling tube, and the mercury, thus displaced, escapes through the overflow-tube *I* to the bottle *H*. By means of an aspirator a rapid current of gas is drawn along the tube *F* which is connected to the flue or gas-main by means of the sampling tube (Fig. 215), a suitable filter being interposed, if necessary, to retain any solid particles. The connection *A*, between the sampling tube and the tube *F*, is preferably made of capillary tubing 3 to 4 inches long, to prevent the diffusion of the gas backwards from *N* to *F*. If desired, a small non-return mercury valve may be inserted at this point.

"To start the apparatus, the tube *F* is connected with the gas supply and a rapid current of gas is drawn through *F* by means of the aspirator.

"The rubber tube connecting the jet *V* with the water-supply is then closed by the clip *S*, and the water is allowed to run into *T* and to overflow freely through *W* the height of which has previously been adjusted to the desired level. Water is now run from the tank *Q* until the top of the overflow-tube *I* is at the level of the shoulder of the gas tube *N*, and *J* and *N* are now filled with mercury by means of a small funnel in *J*. The capillary *A* is finally filled with mercury by raising the reservoir *J*, the lower stopcock of the sampling-tube is closed, and *J* is then lowered to its former position and filled to the overflow-tube with mercury; the operation of sampling may now be commenced by opening the lower stopcock of the gas tube *N* and starting the flow of water from the jet. The aspirator and the water-supply to *T* remain in operation during the whole period of the test and the apparatus requires no further attention.

"The period of sampling may be varied in a number of different ways:

(1) "Jets may be constructed to deliver the requisite quantity of water in specified times; these are easily drawn from glass tubing in a blowpipe-flame, the final adjustment being effected by altering the head of water in *T*.

(2) "Tanks of various diameters may be employed.

(3) "The height of the sampling tube *N* may be varied."

#### REFERENCES

- Sinnatt, F. S., "A Convenient Apparatus for Obtaining an Average Sample of Gas and for Regulating the Flow of a Gas into an Evacuated Vessel." *Analyst*, 37, p. 250,  
Gray, Thomas, "An Automatic Gas Sampling Apparatus." *J. Soc. Chem. Ind.*, 32, p. 1092.  
White, "Gas and Fuel Analysis." International Chemical Series.

The author desires to acknowledge his indebtedness to J. S. Coye for his assistance in preparation of this chapter.



## MISCELLANEOUS\*

### ALCOHOL

#### Detection and Estimation of Alcohol

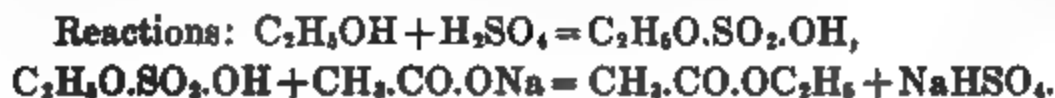
**Detection of Alcohol.** Ethyl or "grain alcohol"  $C_2H_5OH$  boils at  $78.4^\circ C$ . so that it readily distills with steam. If an appreciable amount of alcohol is present in the liquor it may be detected by the odor of the solution or in the first fraction of its distillate.

**Iodoform Test.** A few cc. of the liquor are distilled and to this distillate is added a small crystal of iodine or a few cc. of aqueous solution of iodine-potassium iodide solution, followed by sufficient potassium hydroxide to give the liquid a distinct yellow to brownish color. The solution is warmed gently. If alcohol is present a whitish to lemon yellow precipitate of iodoform will appear. The odor of iodoform may be noted. If the crystals form slowly they are deposited in form of perfect stars and hexagonal plates. This test is not conclusive of alcohol as other organic materials also give iodoform.

**Berthelot's Test.** The distillate of the liquid is vigorously agitated with a few drops of benzoyl chloride and 4 or 5 drops of 10% solution of sodium hydroxide, until the penetrating odor of benzoyl chloride has disappeared. The characteristic odor of ethyl benzoate will be detected if alcohol is present in the liquid tested.



**Ethyl Acetate Test.** The liquid (distillate) is mixed with the same volume of concentrated sulphuric acid. A very small quantity of anhydrous (fused) sodium acetate is added and the mixture warmed. The odor of ethyl acetate will be recognized if alcohol was present in the liquid tested.



#### Determination of Alcohol

In carbonated liquids the carbon dioxide should first be expelled by pouring the liquor back and forth from one beaker to another, or by vigorously shaking the sample in a large separatory funnel and drawing off the lower portion, repeating this several times if necessary. After treatment the liquid should be free from foam.

**Distillation Method.** This is the most accurate method for determination of alcohol. A convenient quantity of the sample is accurately measured or weighed, according to whether the per cent by weight or measure is desired.

\*Edited by Wilfred W. Scott.

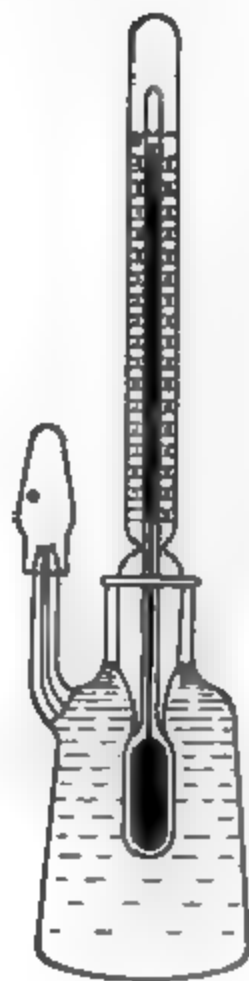


FIG. 221. Pycnometer.

The weight taken varies from 25 to 100 grams, according to the alcohol content of the sample.

The sample is placed in a 250 to 400 cc. round-bottom flask and diluted to 150 cc. The flask is connected to a condenser and 90 to 95 cc. of the liquid is distilled into a narrow-necked flask. The distillate is made to exactly 100 cc. with distilled water.

The specific gravity of the thoroughly mixed distillate is taken by means of the pycnometer or by the Westphal balance, the temperature of the liquid being exactly 15.6° C. From the specific gravity the corresponding percentage of alcohol by weight or by volume, or the grams per 100 cc. in the distillate, is ascertained from the accompanying tables.

The percentage of alcohol by weight in the sample is obtained by multiplying the per cent by weight in the distillate by the weight of the distillate, and dividing by the weight of the sample taken. The per cent by volume is obtained by multiplying the per cent by volume in the distillate by 100 and dividing by the volume of the sample taken.

**Evaporation Method.** Should a distillation apparatus not be available the following method may be used. The specific gravity of the original sample is determined, the temperature being regulated to 15.6° C. A measured portion of the liquor (50–100 cc.) is placed in a porcelain dish over a water bath and three fourths of its volume evaporated off. The concentrate is diluted to exactly its original volume and its specific gravity again taken at 15.6° C. To apply the table add 1 to the original specific gravity and from this total subtract the second specific gravity. The difference is the specific gravity corresponding to the alcohol in the liquor. For example if the specific gravity of the original solution was 0.9989 and the de-alcoholized sample was 1.0005. Then  $1.9989 - 1.0005 = .9984 = 1.06\%$  alcohol, by volume.

If the liquor is free from residue its specific gravity may be taken directly without distillation and the alcohol content determined, provided it is a mixture of water and alcohol.

### **Analysis of Grain Alcohol (Ethyl Alcohol, Spirits of Wine, Cologne Spirits)**

**Per cent Ethyl Alcohol.** The method of determining per cent of alcohol by the distillation of the alcohol from liquors has already been discussed. In straight grain alcohol the specific gravity may be taken directly by means of the Westphal balance or by means of the pycnometer and the amount of alcohol by weight or volume obtained from the tables on page 1526.

*Proof.* This is obtained by multiplying the per cent by volume of the ethyl alcohol by 2.

**Non-volatile Residue.** 100 cc. of the sample, in a large platinum (tared) dish are evaporated on the water bath to a moist residue. The evaporation to dryness is accomplished in a water oven for two and a half hours at 100° C. The weight of the residue divided by the specific gravity gives per cent of non-volatile residue.

**Acidity Expressed as Acetic Acid.** 10 cc. of the alcohol are titrated with N/10 NaOH in presence of phenolphthalein indicator.

1 cc. N/10 NaOH = 0.006 gram acetic acid.

**Distilled Solution for Determining Aldehydes, Furfural and Esters (A).** To 250 cc. of the sample 30 cc. of water are added and the liquor distilled into a 250 cc. volumetric flask. When the distillate has almost reached the mark the distillation is discontinued and the volume made up to mark by addition of water. The distillate contains all the aldehyde, furfural and esters. 1 cc. of this solution is equivalent to 1 cc. of the original sample.

## ALDEHYDES

### Qualitative Examination

**Alkaline Silver Nitrate Reagent.** Three grams of  $\text{AgNO}_3$  are dissolved in a little water in a 100 cc. volumetric flask, 3 grams of pure  $\text{NaOH}$  are added followed by 20 cc. of strong  $\text{NaOH}$  and the whole made to 100 cc.

**Test.** Ten cc. of the sample are diluted with an equal volume of water in a glass stoppered bottle, 1 cc. of the alkaline silver reagent added, and the bottle is closed and placed in a dark chamber for an hour. The liquid is now filtered and the filtrate made acid with  $\text{HNO}_3$  and a few drops of  $\text{HCl}$  added. A precipitate of  $\text{AgCl}$  indicates the non-reduction of the silver salt and consequently a negligible amount of aldehyde in the sample.

### Quantitative Determination of Aldehyde

**Reagents. Alcohol—Aldehyde-free.** To 1.5 liters of 95% ethyl alcohol are added 25 grams of  $\text{NaOH}$  in a large distilling flask and all but 100 cc. distilled over. To this distillate are added 2.5 grams of meta-phenylenediamine hydrochloride, the sample being placed in a large flask with reflux condenser. After heating on a steam bath for several hours the solution is distilled down to about 200 cc. The distillate (rejecting the first 100 cc.) is placed in a stoppered bottle for use.

**Fuchsin-Sulphite Solution.** To 0.5 gram of fuchsin dissolved in 500 cc. of water are added 5 grams of  $\text{SO}_2$  dissolved in water. (100 cc.  $\text{H}_2\text{O}$  saturated with  $\text{SO}_2$  at  $20^\circ \text{C}$ . contains 11.29 g.  $\text{SO}_2$ , at  $15^\circ \text{C}$ . = 13.5 g.  $\text{SO}_2$ —Seidell. Determine by titrating with N/10 iodine sol. 1 cc. = .0032 g.  $\text{SO}_2$ .) Dilute to 1000 cc. and allow to stand until colorless. The solution retains its strength only a few days, so should be made up in small quantities at a time.

**Standard Acetaldehyde Solution.** Five grams of aldehyde ammonia are purified by repeated extraction with ether, grinding the salt with the ether in a mortar and decanting off the ether. The salt is dried by blowing air over it and finally placing it in a vacuum desiccator over strong  $\text{H}_2\text{SO}_4$ . 1.386 gram of the purified salt is dissolved in 50 cc. of the 95% alcohol reagent prepared as stated above. To this are added 22.7 cc. of N alcoholic  $\text{H}_2\text{SO}_4$  (49.04 grams  $\text{H}_2\text{SO}_4$  made up to 1000 cc. with 95% alcohol) and the solution made to 100 cc. with 95% alcohol. To compensate for the  $(\text{NH}_4)_2\text{SO}_4$  precipitated 0.8 cc. alcohol is added. After standing all night the solution is filtered. 100 cc. of this reagent contains 1 gram of acetaldehyde. It retains its strength.

**Reagent for Standard.** Two cc. of the above solution diluted with 50% alcohol to 100 cc. 1 cc. contains 0.0002 gram acetaldehyde. Make up fresh for use.

### Procedure for Aldehydes

Ten cc. of the solution *A* are diluted to 50 cc. with the aldehyde free alcohol (diluted to 50% by volume) 25 cc. of fuchsin reagent are added and the mixture allowed to stand for 15 minutes (all reagents and the sample should be at 15° C.). The solution is now compared colorimetrically with standards made up in the same way. Nessler tubes may be used. Comparison may be made in a colorimeter. From this the per cent aldehyde is readily calculated.

### Determination of Furfural

**Standard Furfural Reagents.** One gram of freshly redistilled furfural is dissolved in 100 cc. 95% alcohol (furfural free). This solution keeps.

One cc. of the strong solution is diluted to 100 cc. with 50% (by volume) alcohol. 1 cc. = 0.0001 gram furfural.

**Procedure.** Twenty cc. of the distilled solution (*A*) are diluted to 50 cc. with 50% (by volume) of furfural-free alcohol. To this are added 2 cc. of colorless aniline and 0.5 cc. of dilute HCl (5 : 4) and the mixture placed in a water bath at 15° C. for fifteen minutes. Colorimetric comparison is now made with standards containing known amounts of furfural, the solutions being prepared in the same way as the sample.

### Determination of Esters Expressed as Ethyl Acetate

Fifty cc. of the distilled solution (*A*) in an Erlenmeyer flask are exactly neutralized with N/10 NaOH (phenolphthalein indicator) and about 50 cc. excess added, the exact amount being recorded. The solution is boiled for an hour with reflux condenser. After cooling, the excess of alkali is titrated with N/10 acid. The cc. N/10 NaOH consumed in the saponification, multiplied by 0.0088 gives the gram weight of esters calculated as ethyl acetate. This weight divided by the specific gravity of the sample and multiplied by 2 gives per cent.

### Determination of Fusel Oil

Fifty cc. of the original sample, in an Erlenmeyer flask, are diluted with an equal volume of water and 20 cc. of N/5 NaOH added. The mixture is now saponified by boiling for an hour with reflux condenser. The flask is connected to a condenser and about 90 cc. distilled into a deep beaker. 25 cc. of water are added to the flask and the distillation continued until the total volume of the distillate is 115 cc. Finely ground salt (NaCl) is now added until the solution is almost saturated and a saturated solution of NaCl added until the specific gravity of the solution is 1.10. The solution placed in a separatory funnel is extracted four times with carbon tetrachloride, CCl<sub>4</sub>, using 40, 30, 20 and 10 cc. CCl<sub>4</sub> respectively. To the extract in a separatory funnel 10 cc. of KOH solution (1 : 1) are added. This solution is cooled in ice water to 0° C. and at the same time 100 cc., accurately measured, of KMnO<sub>4</sub> solution (20 grams per liter) in a flask. When cooled to 0° C. the bulk of the KMnO<sub>4</sub> solution is added to the extract, leaving the rinsing out of the flask until later. The mixture removed from the ice bath is shaken vigorously for five minutes,

then set aside for half an hour allowing it to warm up to room temperature (20–25° C.).

Into a liter Erlenmeyer flask are measured accurately 100 cc. of  $\text{H}_2\text{O}_2$  solution (2% stronger than the  $\text{KMnO}_4$  solution) followed by 100 cc. of 25%  $\text{H}_2\text{SO}_4$  and to this mixture are added slowly the contents of the separatory funnel, swirling to get an even distribution. (The acid solution should be constantly in excess.) The rinsing of the separatory funnel and the flask containing the residue of the  $\text{KMnO}_4$  are added and the excess of the  $\text{H}_2\text{O}_2$  determined by titration with standard  $\text{KMnO}_4$  solution (10 grams  $\text{KMnO}_4$  per liter).

**Blank.** The same amounts of stronger  $\text{KMnO}_4$ ,  $\text{KOH}$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  are mixed side by side with the sample and the residual  $\text{H}_2\text{O}_2$  determined with the standard  $\text{KMnO}_4$  to determine the blank. This is subtracted from the first titration and the difference multiplied by the value of the standard  $\text{KMnO}_4$ . If this is exactly 10 grams per liter as determined by titration with N  $\text{H}_2\text{C}_2\text{O}_4$  then—

1 cc.  $\text{KMnO}_4$  = 0.696 gram amyl alcohol. ( $\text{KMnO}_4$  10 g. per liter.)

**NOTE.** 1 cc. N  $\text{H}_2\text{C}_2\text{O}_4$  = 0.03161 g.  $\text{KMnO}_4$ . The standard  $\text{KMnO}_4$  should contain 0.01 g. per cc. of the reagent.

### Detection of Nitrates in Grain Alcohol

Fifty cc. of the sample are neutralized with N/10  $\text{NaOH}$  (phenolphthalein indicator) and evaporated to a moist residue. A little distilled water is added and 1 cc. of phenoldisulphonic acid and the mix made alkaline with  $\text{NH}_4\text{OH}$ . A bright orange color indicates the presence of nitrates. Run a blank on the water used. See subject of nitrates in the chapter of Water.

### Determination of Sulphur Compounds in Grain Alcohol

A hundred cc. of the alcohol are made slightly alkaline with N/10  $\text{NaOH}$  (phenolphthalein) and 5 cc.  $\text{H}_2\text{O}_2$  added, preferably in a large platinum dish. The residue is ignited over an alcohol flame then taken up with 50 cc. of water, 5 cc. dilute  $\text{HCl}$  added and 5 cc. 10%  $\text{BaCl}_2$ . The precipitated  $\text{BaSO}_4$  is filtered off, ignited and weighed according to the customary procedure.

$$\text{BaSO}_4 \times 0.1373 = \text{S.}$$

### Determination of Methyl Alcohol, Wood Spirit, Wood Naphtha, Wood Alcohol, Etc.

See Methyl Alcohol in section following the tables on alcohol.



## PERCENTAGE OF ALCOHOL BY VOLUME AND BY WEIGHT\*

GILPIN, DRINKWATER, AND SQUIBB

Specific Gravity at 60° F.	Alcohol			Specific Gravity at 60° F.	Alcohol		
	per cent by volume.	per cent by weight.	Grams per 100 cc.		per cent by volume.	per cent by weight.	Grams per 100 cc.
1 00000	0 00	0 00	0 00	.99473	3.60	2 88	2.88
0 99984	0.10	0.08	0 08	.99459	3.70	2.96	2.94
.99968	0.20	0.16	0.16	.99445	3.80	3.04	3.02
.99953	0 30	0.24	0.24	.99431	3.90	3.12	3.10
.99937	0 40	0.32	0.32	.99417	4.00	3.20	3.18
.99923	0.50	0.40	0.40	.99403	4.10	3.28	3.26
.99907	0.60	0 48	0.48	.99390	4.20	3.36	3.34
.99892	0 70	0 56	0 56	.99376	4 30	3.44	3.42
.99877	0.80	0 64	0.64	.99363	4.40	3.52	3.50
.99861	0.90	0.71	0.71	.99349	4.50	3.60	3.58
.99849	1 00	0 79	0.79	.99335	4 60	3 68	3.66
.99834	1.10	0.87	0.87	.99322	4 70	3 76	3.74
.99819	1.20	0 95	0.95	.99308	4.80	3 84	3.81
.99805	1.30	1 03	1.03	.99295	4.90	3 92	3.89
.99790	1 40	1 11	1.11	.99281	5 00	4 00	3.97
.99775	1.50	1.19	1.19	.99268	5.10	4 08	4.05
.99760	1.60	1.27	1.27	.99255	5 20	4 16	4.13
.99745	1 70	1 35	1.35	.99241	5 30	4 24	4.21
.99731	1.80	1 43	1.43	.99228	5.40	4.32	4.29
.99716	1.90	1.51	1.51	.99215	5.50	4 40	4.37
.99701	2 00	1 59	1 59	.99202	5.60	4.48	4.44
.99687	2 10	1 67	1.66	.99189	5 70	4.56	4.52
.99672	2.20	1 75	1.74	.99175	5 80	4.64	4.60
.99658	2 30	1 83	1 82	.99162	5.90	4.72	4.68
.99643	2 40	1 91	1 90	.99149	6 00	4.80	4.76
.99629	2 50	1.99	1 98	.99136	6 10	4.88	4.84
.99615	2.60	2.07	2.06	.99123	6.20	4 96	4.92
.99600	2 70	2 15	2.14	.99111	6 30	5.05	5.00
.99586	2 80	2 23	2 22	.99098	6 40	5.13	5.08
.99571	2 90	2.31	2.30	.99085	6.50	5.21	5.16
.99557	3.00	2 39	2 38	.99072	6.60	5 29	5.24
.99543	3 10	2.47	2 46	.99059	6.70	5.37	5.32
.99529	3 20	2.55	2 54	.99047	6 80	5 45	5.40
.99515	3 30	2 64	2 62	.99034	6 90	5.53	5.48
.99501	3 40	2 72	2 70	.99021	7.00	5.61	5.56
.99487	3.50	2.80	2 78	.99009	7.10	5 69	5.64
.98996	7 20	5 77	5 72	.98513	11.30	9 11	8 97
.98984	7 30	5 86	5 80	.98502	11.40	9.19	9 05
.98971	7.40	5.94	5.88	.98491	11.50	9 27	9.13
.98959	7 50	6 02	5 96	.98479	11.60	9.35	9 21
.98947	7 60	6 10	6 04	.98468	11.70	9 43	9.29
.98934	7 70	6 18	6 11	.98457	11.80	9.51	9.36
.98922	7 80	6.26	6 19	.98446	11.90	9 59	9.44
.98909	7 90	6 34	6 27	.98435	12.00	9.67	9 52
.98897	8 00	6 42	6 35	.98424	12.10	9.75	9 60
.98885	8 10	6 50	6.43	.98413	12.20	9 83	9.68
.98873	8.20	6 58	6.51	.98402	12.30	9 92	9.76
.98861	8.30	6 67	6 59	.98391	12.40	10 00	9 84
.98849	8 40	6 75	6 67	.98381	12.50	10 08	9.92
.98837	8.50	6.83	6.75	.98370	12.60	10.16	10.00

\* Bulletin No. 65, U. S. Department of Agriculture.

## PERCENTAGE OF ALCOHOL BY VOLUME AND BY WEIGHT

(Continued)

Specific Gravity at 60° F.	Alcohol			Specific Gravity at 60° F.	Alcohol		
	per cent by volume	per cent by weight	Grams per 100 cc.		per cent by volume	per cent by weight	Grams per 100 cc.
.98825	8.60	6.91	6.83	.98359	12.70	10.24	10.07
.98813	8.70	6.99	6.91	.98348	12.80	10.33	10.15
.98801	8.80	7.07	6.99	.98337	12.90	10.41	10.23
.98789	8.90	7.15	7.07	.98326	13.00	10.49	10.31
.98777	9.00	7.23	7.14	.98315	13.10	10.57	10.39
.98765	9.10	7.31	7.22	.98305	13.20	10.65	10.47
.98754	9.20	7.39	7.30	.98294	13.30	10.74	10.55
.98742	9.30	7.48	7.38	.98283	13.40	10.82	10.63
.98730	9.40	7.56	7.46	.98273	13.50	10.90	10.71
.98719	9.50	7.64	7.54	.98261	13.60	10.98	10.79
.98707	9.60	7.72	7.62	.98251	13.70	11.06	10.87
.98695	9.70	7.80	7.70	.98240	13.80	11.15	10.95
.98683	9.80	7.88	7.78	.98230	13.90	11.23	11.03
.98672	9.90	7.96	7.85	.98219	14.00	11.31	11.11
.98660	10.00	8.04	7.93	.98208	14.10	11.39	11.19
.98649	10.10	8.12	8.01	.98198	14.20	11.47	11.27
.98637	10.20	8.20	8.09	.98188	14.30	11.56	11.35
.98626	10.30	8.29	8.17	.98177	14.40	11.64	11.43
.98614	10.40	8.37	8.25	.98167	14.50	11.72	11.51
.98603	10.50	8.45	8.33	.98156	14.60	11.80	11.59
.98592	10.60	8.53	8.41	.98146	14.70	11.88	11.67
.98580	10.70	8.61	8.49	.98135	14.80	11.97	11.75
.98569	10.80	8.70	8.57	.98125	14.90	12.05	11.82
.98557	10.90	8.78	8.65	.98114	15.00	12.13	11.90
.98546	11.00	8.86	8.73	.98104	15.10	12.21	11.98
.98535	11.10	8.94	8.81	.98093	15.20	12.29	12.06
.98524	11.20	9.02	8.89	.98082	15.30	12.38	12.14
.98073	15.40	12.46	12.22	.97658	19.50	15.84	15.47
.98063	15.50	12.54	12.30	.97648	19.60	15.93	15.55
.98052	15.60	12.62	12.37	.97638	19.70	16.01	15.63
.98042	15.70	12.70	12.45	.97628	19.80	16.09	15.71
.98032	15.80	12.79	12.53	.97618	19.90	16.18	15.79
.98021	15.90	12.87	12.61	.97608	20.00	16.26	15.87
.98011	16.00	12.95	12.69	.97598	20.10	16.34	15.95
.98001	16.10	13.03	12.77	.97588	20.20	16.42	16.03
.97991	16.20	13.12	12.85	.97578	20.30	16.51	16.10
.97980	16.30	13.20	12.93	.97568	20.40	16.59	16.18
.97970	16.40	13.29	13.01	.97558	20.50	16.67	16.26
.97960	16.50	13.37	13.09	.97547	20.60	16.75	16.34
.97950	16.60	13.45	13.17	.97537	20.70	16.84	16.42
.97940	16.70	13.53	13.25	.97527	20.80	16.92	16.50
.97929	16.80	13.62	13.33	.97517	20.90	17.01	16.58
.97919	16.90	13.70	13.41	.97507	21.00	17.09	16.66
.97909	17.00	13.78	13.49	.97497	21.10	17.17	16.74
.97899	17.10	13.86	13.57	.97487	21.20	17.26	16.82
.97889	17.20	13.94	13.65	.97477	21.30	17.34	16.90
.97879	17.30	14.03	13.73	.97467	21.40	17.43	16.98
.97869	17.40	14.11	13.81	.97457	21.50	17.51	17.06
.97859	17.50	14.19	13.89	.97446	21.60	17.59	17.14
.97848	17.60	14.27	13.96	.97436	21.70	17.67	17.22
.97838	17.70	14.35	14.04	.97426	21.80	17.76	17.30
.97828	17.80	14.44	14.12	.97416	21.90	17.84	17.38
.97818	17.90	14.52	14.20	.97406	22.00	17.92	17.46

## PERCENTAGE OF ALCOHOL BY VOLUME AND BY WEIGHT

(Continued)

Specific Gravity at 60° F.	Alcohol			Specific Gravity at 60° F.	Alcohol		
	per cent by volume.	per cent by weight.	Grams per 100 cc.		per cent by volume.	per cent by weight.	Grams per 100 cc.
.97808	18.00	14.60	14.28	.97396	22.10	18.00	17.54
.97798	18.10	14.68	14.36	.97386	22.20	18.09	17.62
.97788	18.20	14.77	14.44	.97375	22.30	18.17	17.70
.97778	18.30	14.85	14.52	.97365	22.40	18.26	17.78
.97768	18.40	14.94	14.60	.97355	22.50	18.34	17.86
.97758	18.50	15.02	14.68	.97345	22.60	18.42	17.94
.97748	18.60	15.10	14.76	.97335	22.70	18.51	18.02
.97738	18.70	15.18	14.84	.97324	22.80	18.59	18.10
.97728	18.80	15.27	14.92	.97314	22.90	18.68	18.18
.97718	18.90	15.38	15.00	.97304	23.00	18.76	18.26
.97708	19.00	15.43	15.08	.97294	23.10	18.84	18.33
.97698	19.10	15.51	15.15	.97283	23.20	18.92	18.41
.97688	19.20	15.59	15.23	.97273	23.30	19.01	18.49
.97678	19.30	15.68	15.31	.97263	23.40	19.09	18.57
.97668	19.40	15.76	15.39	.97253	23.50	19.17	18.65
.97242	23.60	19.25	18.73	.96805	27.70	22.71	21.98
.97232	23.70	19.34	18.81	.96794	27.80	22.79	22.06
.97222	23.80	19.42	18.88	.96783	27.90	22.88	22.14
.97211	23.90	19.51	18.96	.96772	28.00	22.96	22.22
.97201	24.00	19.59	19.04	.96761	28.10	23.04	22.30
.97191	24.10	19.67	19.12	.96749	28.20	23.13	22.38
.97180	24.20	19.76	19.20	.96738	28.30	23.21	22.45
.97170	24.30	19.84	19.28	.96726	28.40	23.30	22.53
.97159	24.40	19.93	19.36	.96715	28.50	23.38	22.61
.97149	24.50	20.01	19.44	.96704	28.60	23.47	22.69
.97139	24.60	20.09	19.52	.96692	28.70	23.55	22.77
.97128	24.70	20.18	19.60	.96681	28.80	23.64	22.85
.97118	24.80	20.26	19.68	.96669	28.90	23.72	22.93
.97107	24.90	20.35	19.76	.96658	29.00	23.81	23.01
.97097	25.00	20.43	19.84	.96646	29.10	23.89	23.09
.97086	25.10	20.51	19.92	.96635	29.20	23.98	23.17
.97076	25.20	20.60	20.00	.96623	29.30	24.06	23.25
.97065	25.30	20.68	20.08	.96611	29.40	24.15	23.33
.97055	25.40	20.77	20.16	.96600	29.50	24.23	23.41
.97044	25.50	20.85	20.24	.96587	29.60	24.32	23.49
.97033	25.60	20.93	20.32	.96576	29.70	24.40	23.57
.97023	25.70	21.02	20.40	.96564	29.80	24.49	23.65
.97012	25.80	21.10	20.47	.96553	29.90	24.57	23.73
.97001	25.90	21.19	20.55	.96541	30.00	24.66	23.81
.96991	26.00	21.27	20.63	.96529	30.10	24.74	23.89
.96980	26.10	21.35	20.71	.96517	30.20	24.83	23.97
.96969	26.20	21.44	20.79	.96505	30.30	24.91	24.04
.96959	26.30	21.52	20.87	.96493	30.40	25.00	24.12
.96949	26.40	21.61	20.95	.96481	30.50	25.08	24.20
.96937	26.50	21.69	21.03	.96469	30.60	25.17	24.28
.96926	26.60	21.77	21.11	.96457	30.70	25.25	24.36
.96915	26.70	21.86	21.19	.96445	30.80	25.34	24.44
.96905	26.80	21.94	21.27	.96433	30.90	25.42	24.52
.96894	26.90	22.03	21.35	.96421	31.00	25.51	24.60
.96883	27.00	22.11	21.43	.96409	31.10	25.60	24.68
.96872	27.10	22.20	21.51	.96396	31.20	25.68	24.76
.96861	27.20	22.28	21.59	.96384	31.30	25.77	24.84
.96850	27.30	22.37	21.67	.96372	31.40	25.85	24.92

## PERCENTAGE OF ALCOHOL BY VOLUME AND BY WEIGHT

(Continued)

Specific Gravity at 60° F.	Alcohol			Specific Gravity at 60° F.	Alcohol		
	per cent by volume.	per cent by weight.	Grams per 100 cc.		per cent by volume.	per cent by weight.	Grams per 100 cc.
.96839	27.40	22.45	21.75	.96360	31.50	25.94	25.00
.96828	27.50	22.54	21.83	.96347	31.60	26.03	25.08
.96816	27.60	22.62	21.90	.96335	31.70	26.11	25.16
.96323	31.80	26.20	25.24	.95787	35.90	29.74	28.49
.96310	31.90	26.28	25.32	.95773	36.00	29.83	28.57
.96298	32.00	26.37	25.40	.95759	36.10	29.92	28.65
.96285	32.10	26.46	25.48	.95745	36.20	30.00	28.73
.96273	32.20	26.54	25.56	.95731	36.30	30.09	28.81
.96260	32.30	26.63	25.64	.95717	36.40	30.17	28.88
.96248	32.40	26.71	25.71	.95703	36.50	30.26	28.96
.96235	32.50	26.80	25.79	.95688	36.60	30.35	29.04
.96222	32.60	26.89	25.87	.95674	36.70	30.44	29.12
.96210	32.70	26.97	25.95	.95660	36.80	30.52	29.20
.96197	32.80	27.06	26.03	.95646	36.90	30.61	29.29
.96185	32.90	27.14	26.11	.95632	37.00	30.70	29.36
.96172	33.00	27.23	26.19	.95618	37.10	30.79	29.44
.96159	33.10	27.32	26.27	.95603	37.20	30.88	29.52
.96146	33.20	27.40	26.35	.95589	37.30	30.96	29.60
.96133	33.30	27.49	26.43	.95574	37.40	31.05	29.68
.96120	33.40	27.57	26.51	.95560	37.50	31.14	29.76
.96108	33.50	27.66	26.59	.95545	37.60	31.23	29.84
.96095	33.60	27.75	26.67	.95531	37.70	31.32	29.92
.96082	33.70	27.83	26.75	.95516	37.80	31.40	30.00
.96069	33.80	27.92	26.82	.95502	37.90	31.49	30.08
.96056	33.90	28.00	26.90	.95487	38.00	31.58	30.16
.96043	34.00	28.09	26.98	.95472	38.10	31.67	30.24
.96030	34.10	28.18	27.06	.95457	38.20	31.76	30.32
.96016	34.20	28.26	27.14	.95442	38.30	31.85	30.40
.96003	34.30	28.35	27.22	.95427	38.40	31.94	30.48
.95990	34.40	28.43	27.30	.95413	38.50	32.03	30.56
.95977	34.50	28.52	27.38	.95398	38.60	32.12	30.64
.95963	34.60	28.61	27.46	.95383	38.70	32.20	30.72
.95950	34.70	28.70	27.54	.95368	38.80	32.29	30.79
.95937	34.80	28.78	27.62	.95353	38.90	32.37	30.87
.95923	34.90	28.87	27.70	.95338	39.00	32.46	30.95
.95910	35.00	28.96	27.78	.95323	39.10	32.55	31.03
.95896	35.10	29.05	27.86	.95307	39.20	32.64	31.11
.95883	35.20	29.13	27.94	.95292	39.30	32.72	31.18
.95869	35.30	29.22	28.02	.95277	39.40	32.81	31.26
.95855	35.40	29.30	28.09	.95262	39.50	32.90	31.34
.95842	35.50	29.38	28.17	.95246	39.60	32.99	31.42
.95828	35.60	29.48	28.25	.95231	39.70	33.08	31.50
.95814	35.70	29.57	28.33	.95216	39.80	33.17	31.58
.95800	35.80	29.65	28.41	.95200	39.90	33.27	31.66
.95185	40.00	33.35	31.74	.94519	44.10	37.02	34.99
.95169	40.10	33.44	31.82	.94502	44.20	37.11	35.07
.95154	40.20	33.53	31.90	.94484	44.30	37.21	35.15
.95138	40.30	33.61	31.98	.94467	44.40	37.30	35.23
.95122	40.40	33.70	32.06	.94450	44.50	37.39	35.31
.95107	40.50	33.79	32.14	.94433	44.60	37.48	35.39
.95091	40.60	33.88	32.22	.94416	44.70	35.57	35.47
.95075	40.70	33.97	32.30	.94398	44.80	37.66	35.55
.95059	40.80	34.06	32.38	.94381	44.90	37.76	35.63

## PERCENTAGE OF ALCOHOL BY VOLUME AND BY WEIGHT\*

(Continued)

Specific Gravity at 60° F	Alcohol			Specific Gravity at 60° F	Alcohol		
	per cent by volume	per cent by weight	Grams per 100 cc.		per cent by volume	per cent by weight	Grams per 100 cc.
.95044	40.90	34.15	32.46	.94304	45.00	37.84	35.71
.95028	41.00	34.24	32.54	.94346	45.10	37.93	35.79
.95012	41.10	34.33	32.62	<del>.94388</del>	45.20	38.02	35.87
.94996	41.20	34.42	32.70	.94311	45.30	38.12	35.95
.94980	41.30	34.50	32.78	.94294	45.40	38.21	<del>36.03</del>
.94964	41.40	34.59	32.86	.94276	45.50	38.30	36.11
.94948	41.50	34.68	32.93	.94258	45.60	38.39	36.19
.94932	41.60	34.77	33.01	.94241	45.70	38.48	<del>36.27</del>
.94916	41.70	34.86	33.09	.94223	45.80	38.57	36.34
.94900	41.80	34.95	33.17	.94206	45.90	38.66	<del>36.42</del>
.94884	41.90	35.04	33.25	.94188	46.00	38.75	<del>36.50</del>
.94868	42.00	35.13	33.33	.94170	46.10	38.84	<del>36.58</del>
.94852	42.10	35.22	33.41	.94152	46.20	38.93	<del>36.66</del>
.94835	42.20	35.31	33.49	.94134	46.30	39.03	36.74
.94810	42.30	35.40	33.57	.94116	46.40	39.12	<del>36.82</del>
.94802	42.40	35.49	33.65	.94098	46.50	39.21	<del>36.90</del>
.94786	42.50	35.58	33.73	<del>.94080</del>	46.60	39.30	<del>36.98</del>
.94770	42.60	35.67	33.81	.94062	46.70	39.39	37.06
.94753	42.70	35.76	33.89	<del>.94044</del>	46.80	39.49	37.13
.94737	42.80	35.85	33.97	.94026	46.90	39.58	37.21
.94720	42.90	35.94	34.04	.94008	47.00	39.67	37.29
.94704	43.00	36.03	34.12	.93990	47.10	39.76	37.37
.94687	43.10	36.12	34.20	.93971	47.20	39.85	37.45
.94670	43.20	36.21	34.28	.93953	47.30	39.95	37.53
.94654	43.30	36.30	34.36	.93934	47.40	40.04	37.61
.94637	43.40	36.39	34.44	.93916	47.50	40.13	37.69
.94620	43.50	36.48	34.52	.93898	47.60	40.22	37.77
.94603	43.60	36.57	34.60	.93879	47.70	40.32	37.85
.94586	43.70	36.66	34.68	.93861	47.80	40.41	37.93
.94570	43.80	36.75	34.76	.93842	47.90	40.51	38.01
.94553	43.90	36.84	34.84	.93824	48.00	40.60	38.09
.94536	44.00	36.93	34.91	.93805	48.10	40.69	38.17
.93786	48.20	40.78	38.25	.93617	49.10	41.61	<del>39.00</del>
.93768	48.30	40.88	38.33	.93598	49.20	41.71	39.04
.93749	48.40	40.97	38.41	.93578	49.30	41.80	39.12
.93730	48.50	41.06	38.49	.93559	49.40	41.90	39.20
.93711	48.60	41.15	38.57	.93540	49.50	41.99	39.28
.93692	48.70	41.24	38.65	.93521	49.60	42.08	39.36
.93679	48.80	41.34	38.72	.93502	49.70	42.18	39.44
.93655	48.90	41.43	38.80	.93482	49.80	42.27	39.52
.93636	49.00	41.52	38.88	.93463	49.90	42.37	<del>39.60</del>

\* See additional tables in Chem. Annual, D. Van Nostrand Co.

## METHYL ALCOHOL

**Detection of Methyl Alcohol—Method of Riche and Bardy<sup>1</sup>**

The following method for the detection of methyl alcohol in commercial spirit of wine depends on the formation of methyl-anilin violet:

Place 10 cc. of the sample, previously rectified over potassium carbonate if necessary, in a small flask with 15 grams of iodine and 2 grams of red phosphorus. Keep in ice water for from ten to fifteen minutes until action has ceased. Distil on a water bath the methyl and ethyl iodides formed into about 30 cc. of water. Wash with dilute alkali to eliminate free iodine. Separate the heavy oily liquid which settles and transfer to a flask containing 5 cc.

of anilin. The flask should be placed in cold water, in case the action should be violent, or, if necessary, the reaction may be stimulated by gently warming the flask. After one hour boil the product with water and add about 20 cc. of a 15 per cent solution of soda; when the bases rise to the top as an oily layer fill the flask up to the neck with water and draw them off with a pipette. Oxidize 1 cc. of the oily liquid by adding 10 grams of a mixture of 100 parts of clean sand, 2 of common salt, and 3 of cupric nitrate; mix thoroughly, introduce into a glass tube, and heat to 90° C. for eight or ten hours. Exhaust the product with warm alcohol, filter, and make up with alcohol to 100 cc. If the sample of spirits be pure the liquid is of a red tint, but in the presence of 1 per cent of methyl alcohol it has a distinct violet shade; with 2.5 per cent the shade is very distinct, and still more so with 5 per cent. To

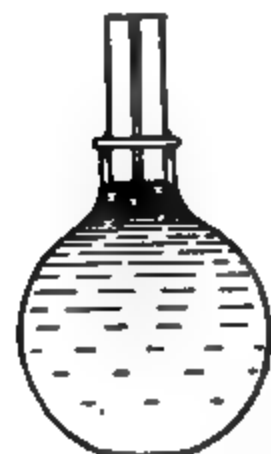


FIG. 222. Pycnometer.

detect more minute quantities of methyl alcohol, dilute 5 cc. of the colored liquid to 100 cc. with water, and dilute 5 cc. of this again to 400 cc. Heat the liquid thus obtained in porcelain and immerse a fragment of white merino (free from sulphur) in it for half an hour. If the alcohol be pure the wool will remain white, but if methylated the fiber will become violet, the depth of tint giving a fair approximate indication of the proportion of methyl alcohol present.

**Detection of Methyl Alcohol—Oxidation Method**

Twenty-five cc. of the sample are diluted to about 100 cc. in a small distillation flask and about 10 grams of chromic acid added. Methyl alcohol, if present, is oxidized to formaldehyde. 15 to 20 cc. of the solution are distilled into a large test tube and a 5 to 10 cc. portion tested for formaldehyde by one of the methods outlined on the following page.

**Estimation of Methyl Alcohol.** The determination is made by means of the immersion refractometer. Details of the procedure may be found in "Food Inspection and Analysis," by A. E. Leach, John Wiley and Sons, or in the publication of official methods by the Association of Official Agricultural Chemists.

**NOTE.** Regulations United States Internal Revenue on Methyl Alcohol used for denaturing ethyl alcohol. See Regulations No. 30, Revised, U. S. Int. Rev., July 15, 1907.

<sup>1</sup> Allen's Commercial Organic Analysis, 3d ed., 1: 80.

## FORMALDEHYDE

Detection of Formaldehyde<sup>1</sup>

**Leach's Test.** The solution in which formaldehyde is suspected, obtained by distillation if necessary, is tested as follows: To a 10 cc. portion, in a casserole, an equal volume of pure milk is added followed by 10 cc. hydrochloric acid (sp. gr. 1.2) containing about 1 cc. of 10% ferric chloride solution per 500 of the acid. The mixture is heated to 80–90° C., the curd being broken up by agitation. A violet-colored solution indicates formaldehyde.

**Hehner's Test.** Five cc. of the solution in a large test tube is mixed with about 50 cc. of pure milk, the tube tilted to a side and strong sulphuric acid carefully added so as to run down the wall of the tube without mixing with the milk. At the juncture of the acid and milk a violet color will appear if aldehyde is present.

**Morphine-Sulphate Test.** To 5 cc. of morphine sulphate reagent [0.5 gram of morphine sulphate in 500 cc. sulphuric acid (sp. gr. 1.82)] a 2 cc. portion of the solution to be tested is added. The presence of formaldehyde is indicated by a violet color that develops on standing.

## Estimation of Formaldehyde in Solution

Formaldehyde,  $\text{HCHO}$ , is a gas sold in aqueous solution (37%  $\text{HCHO}$  or over). The solution generally contains alcohol to prevent polymerization.

## Determination of Formaldehyde

**Hydrogen Peroxide Method.<sup>2</sup>** To 50 cc. of normal  $\text{NaOH}$  in an Erlenmeyer flask are added 50 cc. of neutral  $\text{H}_2\text{O}_2$  (3% sol.) and 3 cc. of the formaldehyde solution under examination, care being taken to add the sample with the tip of the measuring pipette near the surface of the reagents. A funnel is placed in the neck of the flask and the mixture heated for five minutes on the steam bath, with occasional shaking. The solution is now cooled, the funnel rinsed down, and the excess of  $\text{N NaOH}$  titrated by normal  $\text{H}_2\text{SO}_4$ , in presence of purified litmus indicator

$$1 \text{ cc. N NaOH} = 0.03002 \text{ gram HCHO.}$$

<sup>1</sup> Carry out the tests with blanks of pure ethyl alcohol and ethyl alcohol containing a little methyl alcohol.

<sup>2</sup> J. Assoc. Official Agr. Chemists, Methods of Analysis (1916), page 75.

## GLYCEROL

There are two recognized methods for the determination of glycerol:

A. Acetin method, depending upon the conversion of glycerol to triacetin by means of acetic anhydride and sodium acetate and a quantitative saponification of the triacetin. This method is recommended by the International Committee on glycerol as giving results nearer the truth and should be employed for crude and refined glycerines of over 40% strength.

B. Bichromate method, which is based on the fact that glycerole is completely oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by  $\text{K}_2\text{Cr}_2\text{O}_7$  in presence of  $\text{H}_2\text{SO}_4$ . The method is applicable for determination of glycerines in soap lyes.

The following procedures are taken from the report as recommended.<sup>1</sup>

Acetin Process for the Determination of Glycerol<sup>2</sup>

## Reagents Required

(A) **Best Acetic Anhydride.** This should be carefully selected. A good sample must not require more than 0.1 cc. normal NaOH for saponification of the impurities when a blank is run on 7.5 cc. Only a slight color should develop during digestion of the blank.

The anhydride may be tested for strength by the following method: Into a weighed stoppered vessel, containing 10 to 20 cc. of water, run about 2 cc. of the anhydride, replace the stopper and weigh. Let stand with occasional shaking, for several hours, to permit the hydrolysis of all the anhydride; then dilute to about 200 cc., add phenolphthalein and titrate with N/1 NaOH. This gives the total acidity due to free acetic acid and acid formed from the anhydride. It is worthy of note that in the presence of much free anhydride a compound is formed with phenolphthalein, soluble in alkali and acetic acid, but insoluble in neutral solutions. If a turbidity is noticed toward the end of the neutralization it is an indication that the anhydride is incompletely hydrolyzed and inasmuch as the indicator is withdrawn from the solution, results may be incorrect.

Into a stoppered weighing bottle containing a known weight of recently distilled aniline (from 10 to 20 cc.) measure about 2 cc. of the sample, stopper, mix, cool and weigh. Wash the contents into about 200 cc. of cold water, and titrate the acidity as before. This yields the acidity due to the original, preformed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated to 100 grams) and double the result, obtaining the cc. N/1 NaOH per 100 grams of the sample. 1 cc. N/NaOH equals 0.0510 anhydride.

(B) **Pure Fused Sodium Acetate.** The purchased salt is again completely fused in a platinum, silica or nickel dish, avoiding charring, powdered quickly and kept in a stoppered bottle or desiccator. It is most important that the sodium acetate be anhydrous.

(C) **A Solution of Caustic Soda for Neutralizing, of about N/1 Strength, Free from Carbonate.** This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide) and allowing to settle until clear, or filtering through an asbestos or

<sup>1</sup> Jour. Ind. Chem. Eng., 3, 679-685, 1911.

<sup>2</sup> Jour. Ind. Eng. Chem., Sept., 1911, pp. 683-685.



paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required.

(D) **N/1 Caustic Soda Free from Carbonate.** Prepared as above and carefully standardized. Some caustic soda solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

(E) **N/1 Acid.** Carefully standardized.

(F) **Phenolphthalein Solution.** 0.5 per cent phenolphthalein in alcohol and neutralized.

### The Method

In a narrow-mouthed flask (preferably round-bottomed), capacity about 120 cc., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25 to 1.5 grams of the glycerine. A Grethan or Lunge pipette will be found convenient. Add about 3 grams of the anhydrous sodium acetate, then 7.5 cc. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside diameter. The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used it should have had a preliminary treatment with hot acetic anhydride vapor.

Heat the contents and keep just boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask.

Allow the flask to cool somewhat, and through the condenser tube add 50 cc. of distilled water free from carbon dioxide at a temperature of about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapors from the flask on adding water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment, bearing in mind that the anhydride in excess is much more effectively hydrolyzed in hot than in cold water. The contents of the flask may be warmed to, but must not exceed, 80° C., until the solution is complete, except a few dark flocks representing organic impurities in the crude. By giving the flask a rotary motion, solution is more quickly effected.

Cool the flask and contents without loosening from the condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off the stopper or ground glass connection into the flask, and filter the contents through an acid-washed filter into a Jena glass flask of about 1 liter capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 cc. of phenolphthalein solution (F), then run in caustic soda solution (C) or (D) until a faint pinkish yellow color appears throughout the solution. This neutralization must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralized, as indicated by the slower disappearance of the color developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon dioxide-free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

Now run in from a burette 50 cc. or a calculated excess of N/1 NaOH (*D*) and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate the excess of NaOH with N/1 acid (*E*) until the pinkish yellow or chosen end-point color just remains.<sup>1</sup> A further addition of the indicator at this point will cause an increase of the pink color; this must be neglected, and the first end-point taken.

From the N/1 NaOH consumed calculate the percentage of glycerol (including acetylizable impurities) after making the correction for the blank test described below.

1 cc. N/1 NaOH = 0.03069 gram glycerol.

The coefficient of expansion for normal solutions is 0.00033 per cc. for each degree centigrade. A correction should be made on this account if necessary.

**Blank Test.** As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride, sodium acetate and water as in the analysis. It is not necessary to filter the solution of the melt in this case, but sufficient time must be allowed for the hydrolysis of the anhydride before proceeding with the neutralization. After neutralization it is not necessary to add more than 10 cc. of the N/1 alkali (*D*), as this represents the excess usually present after the saponification of the average soap lye crude. In determining the acid equivalent of the N/1 NaOH, however, the entire amount taken in the analysis, 50 cc., should be titrated after dilution with 300 cc. water free from carbon dioxide and without boiling.

**Determination of the Glycerol Value of the Acetylizable Impurities.** The total residue at 160° C. is dissolved in 1 or 2 cc. of water, washed into the acetylizing flask and evaporated to dryness. Then add anhydrous sodium acetate and acetic anhydride in the usual amounts and proceed as described in the regular analysis. After correcting for the blank, calculate the result to glycerol.

#### Instructions for Calculating the Actual Glycerol Content

(1) Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylizable impurities if any are present.

(2) Determine the total residue at 160° C.

(3) Determine the acetin value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylizable impurities are present these are included in this figure.

Trimethylenglycol is more volatile than glycerine and can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and bichromate results on such distillates. The spread multiplied by 1.736 will give the glycol.

<sup>1</sup> A precipitate at this point is an indication of the presence of iron or alumina, and high results will be obtained unless a correction is made as described below.

**Bichromate Process for Glycerol Determination. Reagents Required**

(A) **Pure potassium bichromate** powdered and dried in air free from dust or organic vapors, at 110° to 120° C. This is taken as the standard.

(B) **Dilute Bichromate Solution.** 7.4564 grams of the above bichromate are dissolved in distilled water and the solution made up to one liter at 15.5° C.

(C) **Ferrous Ammonium Sulphate.** It is never safe to assume this salt to be constant in composition and it must be standardized against the bichromate as follows: dissolve 3.7282 grams of bichromate (A) in 50 cc. of water. Add 50 cc. of 50 per cent. sulphuric acid (by volume), and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute bichromate (B). Calculate the value of the ferrous salt in terms of bichromate.

(D) **Silver Carbonate.** This is prepared as required for each test from 140 cc. of 0.5 per cent. silver sulphate solution by precipitation with about 4.9 cc. N/1 sodium carbonate solution (a little less than the calculated quantity of N/1 sodium carbonate should be used as an excess prevents rapid settling). Settle, decant and wash once by decantation.

(E) **Subacetate of Lead.** Boil a 10 per cent. solution of pure lead acetate with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(F) **Potassium Ferricyanide.** A very dilute, freshly prepared solution containing about 0.1 per cent.

**The Method**

Weigh 20 grams of the glycerine, dilute to 250 cc. and take 25 cc. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes, and add a slight excess (about 5 cc. in most cases) of the basic lead acetate (E), allow to stand a few minutes, dilute with distilled water to 100 cc., and then add 0.15 cc. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 cc., and return the filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate (in the great majority of cases 5 cc. are ample, but occasionally a crude will be found requiring more, and in this case another aliquot of 25 cc. of the dilute glycerine should be taken and purified with 6 cc. of the basic acetate). Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 cc. of the clear filtrate into a flask or beaker (previously cleaned with potassium bichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3.7282 grams of the powdered potassium bichromate (A). Rinse down the bichromate with 25 cc. of water and let stand with occasional shaking until all the bichromate is dissolved (no reduction will take place in the cold).

Now add 50 cc. of 50 per cent. sulphuric acid (by volume) and immerse the vessel in boiling water for two hours and keep protected from dust and organic vapors, such as alcohol, till the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (C), making spot tests on a porcelain plate with the potassium ferricyanide (F). Titrate

back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

1 gram glycerol = 7.4564 grams bichromate.

1 gram bichromate = 0.13411 gram glycerol.

The percentage of glycerol obtained above includes any oxidizable impurities present after the purification. A correction for the non-volatile impurities may be made by running a bichromate test on the residue at 160° C.

For complete analysis see *Journal of Industrial and Engineering Chemistry*, Sept., 1911, pages 679-683.

NOTES. (1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

(2) Before the bichromate is added to the glycerine solution it is essential that the slight excess of lead be precipitated with sulphuric acid, as stipulated.

(3) For crudes practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0.5 cc.

(4) It is sometimes advisable to add a little potassium sulphate to insure a clear filtrate.

## ACETONE

### Analysis of Acetone by Messinger's Method

An amount of acetone in aqueous solution, equivalent to 30-40 mg. is pipetted or added to 50 cc. of N sodium hydroxide solution contained in a glass bottle which can be closed with a ground glass stopper. After standing for 5 minutes, about 25% excess of a 0.1 N solution of iodine is run in from a burette with continual shaking. It is essential to shake properly or to keep the liquid in continuous rotation. The excess of iodine is needed to complete the reaction.<sup>1</sup> The bottle is then stoppered and the solution allowed to stand for at least 10 minutes (20 minutes in cold weather).

Twenty-five cc. of 2 N sulphuric acid is then added from a measuring cylinder, 0.3-0.4 cc. being added in excess of the amount found necessary to neutralize the 50 cc. of caustic soda solution. A 0.05 N solution of sodium thiosulphate is then added from a burette until the yellow color just remains visible. Freshly prepared starch solution is now added and the titration finished. 1 cc. of 0.1 N iodine = 0.96747 mg. of acetone.

If a larger excess of sulphuric acid is added, too much thiosulphate is required, and the real amount of iodine solution required is thus reduced (see below).

If the bottle is not shaken vigorously while adding the iodine solution, the iodine cannot act completely on the acetone.

<sup>1</sup> L. F. Goodwin, *Jour. Am. Chem. Soc.*, 42, 39-45 (Jan., 1920).

TANNIC ACID<sup>1</sup>

The following procedure is applicable for the examination of pure tannic acid solutions and tannins.

## Reagents

**Potassium Permanganate.** Approximately N/10  $\text{KMnO}_4$ . Standardize against N/10 oxalic acid solution.

**Indigo Carmin Solution.** 5 grams of pure indigo carmin dissolved in water, 50 grams of conc.  $\text{H}_2\text{SO}_4$  are added and the solution diluted to 1000 cc.

**Gelatin Solution.** 20 grams of pure gelatine dissolved in hot water and diluted to 1 liter.

**Saturate NaCl Acid Solution.** 5 per cent  $\text{H}_2\text{SO}_4$  solution saturated with NaCl.

## Total Astringency—Lowenthal-Proctor Method

**Standardization of the Indigo Carmin Solution.** The filtered solution should give a yellow color free from brown when oxidized with  $\text{KMnO}_4$ .

Twenty-five cc. of the reagent in a porcelain casserole are diluted to 750 cc. with water and the  $\text{KMnO}_4$  reagent added drop by drop from a burette with constant stirring until a pure yellow color is obtained. The rate of titration should be uniform in all tests and should be carried out very cautiously as the endpoint is approached. This is recognized by a faint pinkish rim appearing, best seen on the shaded side of the casserole.

**Procedure for Astringency.** 1 gram of solid (or 2–5 grams of solution sumac extract) is dissolved in water and diluted to 1 liter. 10 cc. of this solution is placed in a large casserole containing 750 cc. of water. 25 cc. of the carmin solution are added and the mixture titrated with N/10  $\text{KMnO}_4$  as described for standardization of the indigo carmin reagent. From this titration the number of cc.  $\text{KMnO}_4$  required by 25 cc. of indigo carmin reagent are subtracted and the difference represents the  $\text{KMnO}_4$  required by the sample. Multiply cc.  $\text{KMnO}_4$  required by sample by 0.004157 = A.

**Astringent Non-tannins.** To 50 cc. of the solution (in an 8 oz. bottle) made as stated in the previous determination are added 25 cc. of 2% gelatin solution and 25 cc. of the saturated NaCl acid reagent followed by 10 grams of china clay. The bottle is stoppered and the mixture shaken for five minutes and then filtered through a dry filter, thus removing the tannins. The filtrate is tested with more gelatin solution to see that the tannin is completely precipitated. (A stronger gelatin solution should be used if tannin is evident and the test repeated with 25 cc. of this.) 20 cc. of the filtrate, equivalent to 10 cc. of the original solution, are titrated with N/10  $\text{KMnO}_4$  exactly as in the preceding test and the cc.  $\text{KMnO}_4$  consumed by the non-tannins is multiplied by the value of the  $\text{KMnO}_4$  (N/10 = 0.004157) and the result recorded as B.

• **Tannic Acid or Tannins.** The difference between the total astringency, calculated as tannin, and the astringent non-tannins gives the amount of tannins, namely result A minus result B = gram tannin. Calculate to percentage.

1 cc. N/10  $\text{KMnO}_4$  = 0.004157 gram tannin.

<sup>1</sup> References: H. R. Proctor, "Leather Industries Laboratory Book of Analytical and Experimental Methods."

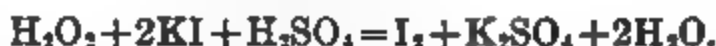
Knecht-Rawson-Lowenthal, "Manual of Dyeing," Vol. II, pp. 802, Eighth Edition. Leach, "Food Inspection and Analysis," p. 282.

## DETERMINATION OF PEROXIDES

## Determination of Hydrogen Peroxide.

Kingzett's Iodide Method<sup>1</sup>

The method depends upon the reaction—



**Procedure.** Approximately 2 grams of potassium iodide are dissolved in 200 cc. of water, conveniently in an Erlenmeyer flask, and 30 cc. of dilute sulphuric acid (1 : 2) are added. Ten cc. of hydrogen peroxide solution (the sample having been diluted to contain approximately 0.6 per cent by weight of  $\text{H}_2\text{O}_2$ ) are run in from a burette, agitating the mixture during the addition. After standing five minutes, the liberated iodine is titrated with N/10 thio-sulphate.

Determination of Hydrogen Peroxide by the Arseneous Acid Method of Jamieson<sup>2</sup>

The method is based on the reactions—



and



**Procedure.** A measured quantity of N/5 solution of  $\text{As}_2\text{O}_3$ , which must be in excess of that required by the peroxide taken for analysis, is placed in a 500 cc. glass stoppered bottle, and 10 cc. of 10% NaOH added, followed by a measured volume of the peroxide from a burette (15–20 cc. of the solution made by diluting 50 cc. of the commercial peroxide to 500 cc.) with gentle agitation of the contents of the bottle. After standing two minutes, 40 cc. of concentrated HCl are added and the stopper inserted in the bottle. The contents of the bottle are shaken violently, holding the stopper in place. The stopper is now cautiously released and the confined gas allowed to escape. Six to seven cc. of chloroform are added and the unoxidized  $\text{As}_2\text{O}_3$  is titrated with N/5  $\text{KIO}_3$  solution, shaking the closed bottle after each addition, until the iodine color in the chloroform has disappeared.

The cc.  $\text{As}_2\text{O}_3$  solution used minus the cc. equivalent of  $\text{KIO}_3$  gives the cc. of arsenous acid required by the hydrogen peroxide.



This method is not influenced by the presence of organic preservatives as is the permanganate method which follows.

\* Selections by W. W. Scott.

<sup>1</sup> J. Chem. Soc., 1880, 792.

<sup>2</sup> Am. Jour. Sci., 44, 150–2 (1917).

**Permanganate Method for Determination of Hydrogen Peroxide**

The procedure depends upon the reaction—



**Procedure.** Fifty cc. of the commercial peroxide are diluted to 500 cc. 10 cc. of this diluted solution are taken for the test. This sample is further diluted to 400 cc. in a beaker, 10 cc. of dilute sulphuric acid (1 : 4) are added and the mixture titrated with N/10  $\text{KMnO}_4$  reagent to a pink coloration.

Should the first drop or of permanganate cause a pink color it indicates that an insufficient quantity of sulphuric acid is present and an additional amount should be added.



**Notes.** If it is required to report the number of volumes of oxygen liberated by one volume of the peroxide "per cent per volume," multiply the per cent weight of  $\text{H}_2\text{O}_2$  by 112 and divide the result by 34.

Since  $\text{H}_2\text{O}_2$  decomposes to  $\text{H}_2\text{O} + \text{O}$ , one gram molecule of peroxide sets free one gram atom of oxygen, equivalent to 11,200 cc. Therefore 100 grams commercial  $\text{H}_2\text{O}_2 = \% \text{H}_2\text{O}_2 \times 11,200$  divided by 34, and 1 gram = 1/100 of this.

# ELECTROMETRIC METHODS OF ANALYSIS

G. L. KELLEY<sup>1</sup> AND J. S. COYE<sup>2</sup>

## The Electrometric Determination of Hydrogen Ion Concentration<sup>2</sup>

The electrometric titration of acids and alkalis is based upon the measurement of the electrode potential between the hydrogen on the surface of a hydrogen electrode and the hydrogen ions in the surrounding solution.

If a bar of any metal is dipped into water, it will immediately give off some positively charged ions, thereby leaving the metal negatively charged. The strength of this charge or resulting potential is determined by two factors: The electrolytic solution pressure of the metal and the osmotic pressure of the ions in the solution.

If two similar electrodes are dipped into two solutions of different concentrations with respect to the metal ions, the electrode which is immersed in the more concentrated solution will receive ions from the solution and be positively charged while the electrode dipping into the less concentrated solution will give off positive ions and become negatively charged relative to the other electrode. This will cause a flow of current from the first electrode to the second if they are externally connected. Such a system constitutes a battery, the total electromotive force of which can be calculated by the following formulae:

The potential difference which is produced by the contact of a metal with a solution of its ions is represented by

$$e = \frac{RT}{NF} \log \frac{P}{p},$$

where  $R$  = gas constant = volts  $\times$  coulombs = 8316 Joules,

$F$  = Faraday = 96,540,

$N$  = valence of the metal,

$P$  = electrolytic solution pressure of the metal,

$p$  = osmotic pressure of the ions in solution,

$T$  = absolute temperature.

Substituting the above values, assuming a temperature of 18° and changing to common logarithms

$$e = \frac{0.058}{N} \log \frac{P}{p}.$$

Since the osmotic pressure is proportional to the concentration of the ions,  $c$  (concentration) may be substituted for  $p$ . Then let  $C$  which represents an ionic concentration which just balances the solution pressure  $P$  be substituted for  $P$  and

$$e = \frac{0.058}{N} \log \frac{C}{c}.$$

This represents a single electrode potential and since the total electromotive force of a cell is the difference between the single electrode potentials

$$E = e_2 - e_1 = \frac{.058}{N} \log \frac{C}{c_2} - \frac{.058}{N} \log \frac{C}{c_1} = \frac{.058}{N} \log \frac{c_1}{c_2}.$$

A platinum or gold electrode, covered with platinum, iridium or palladium

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<sup>2</sup> J. S. Coye, assistant chemist, General Chemical Company.



black and immersed in an atmosphere of hydrogen, acts as if the hydrogen were a metal and is called a hydrogen electrode. The platinum itself is chemically inert and the electrode potential is due to the contact between the concentration of the hydrogen on the electrode surface and the concentration of the hydrogen ions in the solution. Since the concentration of the hydrogen on the electrode surface can be maintained constant by being kept saturated by the hydrogen gas at a constant pressure and temperature, a potential change will be due to a change of hydrogen ion concentration in the solution and, consequently, the e.m.f. is a direct function of the hydrogen ion concentration of the solution and thus its acidity or alkalinity. Now if one hydrogen electrode dips into a solution having a known hydrogen ion concentration of one and a second into a solution of unknown hydrogen ion concentration and the two solutions are connected by a salt bridge (saturated solution of potassium chloride) the total electromotive force will be

$$E = .058 \log \frac{1}{C},$$

and a measurement of the e.m.f. furnishes a means by which the hydrogen ion concentration of the unknown solution can be determined.

In practice it is more convenient to use the more constant calomel electrode instead of a hydrogen electrode having a hydrogen ion concentration of one. The potential of the calomel electrode has been determined in terms of the normal hydrogen electrode, *e.g.*, the 0.1 N calomel electrode has a potential of .337 volts greater than the normal hydrogen electrode at 25° C.

Therefore, by measuring the electromotive force of the system,  
0.1 N calomel electrode / saturated solution of KCl / hydrogen electrode / solution of  $H^+$ -ions at 25° C.

$$E = .05816 \log \frac{1}{C} + .337$$

and the hydrogen ion concentration can be readily calculated, or

$$\frac{E - .337}{.05816} = \log \frac{1}{C}.$$

The value  $\log (1/C)$  is widely used to characterize the hydrogen ion concentration without solving for  $C$  and has been generally designated  $P_H$ . When making an electrometric titration of an acid or a base by means of the hydrogen electrode, this value  $P_H$  or the value  $E$  in volts may be plotted against the number of cc. of acid or alkali used in the titration and a curve obtained from which the endpoint may be readily observed. Figure 1 shows two such curves. Curve V was obtained by titrating a solution of phosphoric acid, to which a slight excess of alkali had been added, with N/10 HCl. Curve VI was then obtained by titrating the resulting solution with N/10 NaOH.

All phosphate exists as disodium phosphate at *B* and as monosodium phosphate at *A*, therefore, the hydrogen ion concentration of disodium and monosodium phosphate solutions may be determined from the e.m.f. at these points. But the principal value of these curves is that they provide a means by which phosphates may be titrated without the use of indicators.

The constants of the above equation are influenced by temperature and by any potential existing between the 0.1 KCl solution of the calomel electrode or the solution being measured and the connecting solution. The latter is practically eliminated by the use of a saturated solution of KCl, while the former may be readily determined and corrections made. It should also be

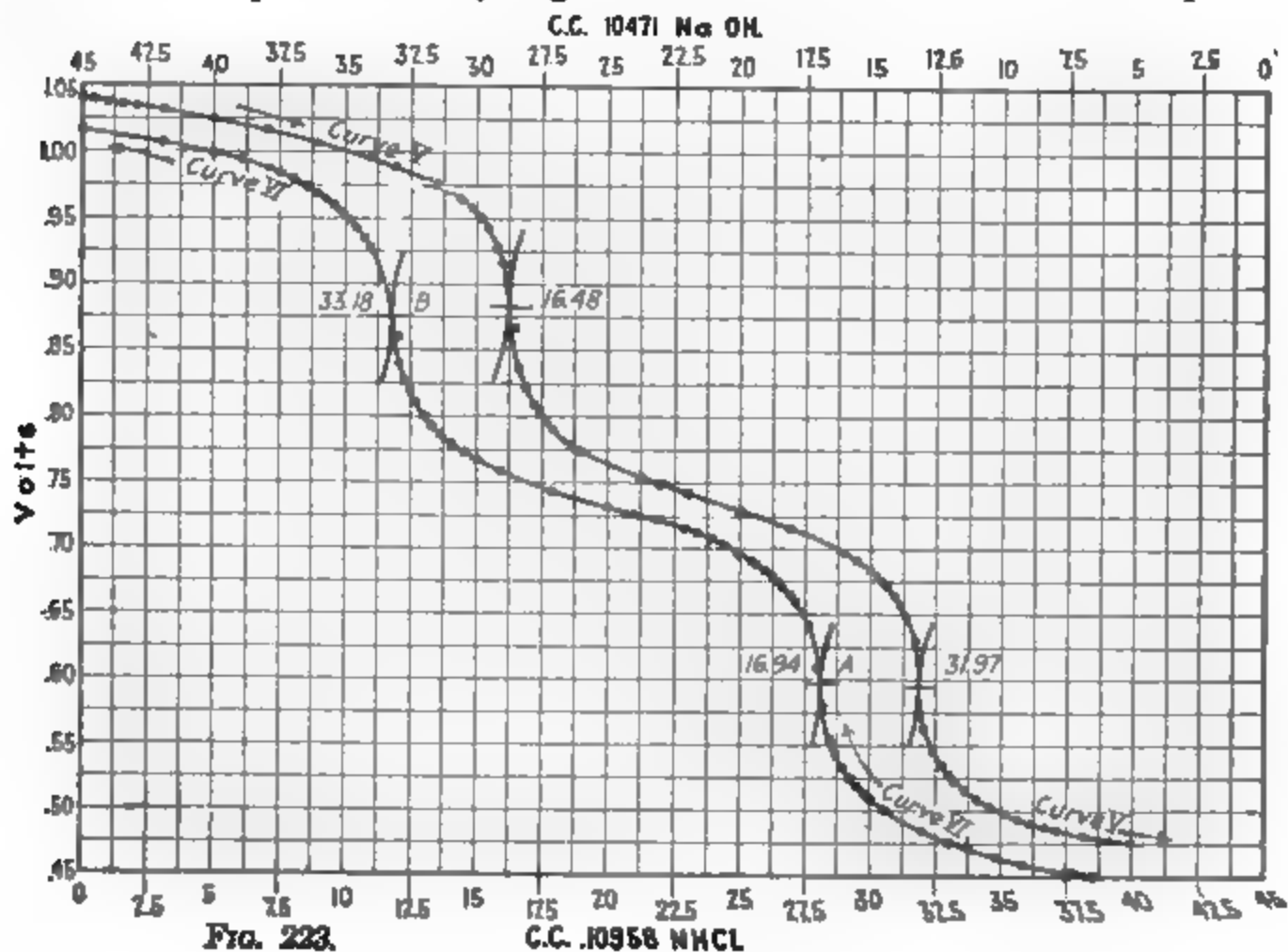
noted that the electrolytic solution tension of the hydrogen is dependent upon the pressure of the gaseous hydrogen at the electrode. 760 mm. partial pressure is the standard pressure for the hydrogen in the standard hydrogen electrode. Corrections for the e.m.f. may be applied for varying hydrogen pressures, but for all work except that of the high precision this may be disregarded.

The hydrogen gas to be used for keeping the hydrogen electrode saturated must be of highest possible purity. Hydrogen generated by electrolyzing a 20% NaOH solution or the ordinary compressed hydrogen from cylinders have been found satisfactory after removing the last traces of oxygen by passing it through heated palladized asbestos or over a heated platinum spiral.

For the measurement of hydrogen ion concentrations a calomel electrode, a hydrogen electrode and a potentiometer for measuring the voltage between them are necessary. For measurements of highest precision a constant temperature bath is also required. Figure 2 shows, diagrammatically, the usual arrangement of apparatus for this work.

The chief advantages of electrometric titrations for hydrogen ion concentration are:

1. The "personal equation," which is always a factor when titrating by means of indicators does not enter into the measurements.
2. Measurements may be made without regard to the opacity of solutions and under poor or troublesome light conditions. Precipitation does not appreciably interfere with the measurement.
3. The method is fundamental. To it all colorimetric methods must be referred for standardization.
4. The potentiometer covers the entire range of hydrogen ion concentrations or  $P_H$  values, whereas any indicator is useful over a limited range only and its particular color change as interpreted by the normal eye in many instances does not correspond to the hydrogen ion concentrations of the true end-point.



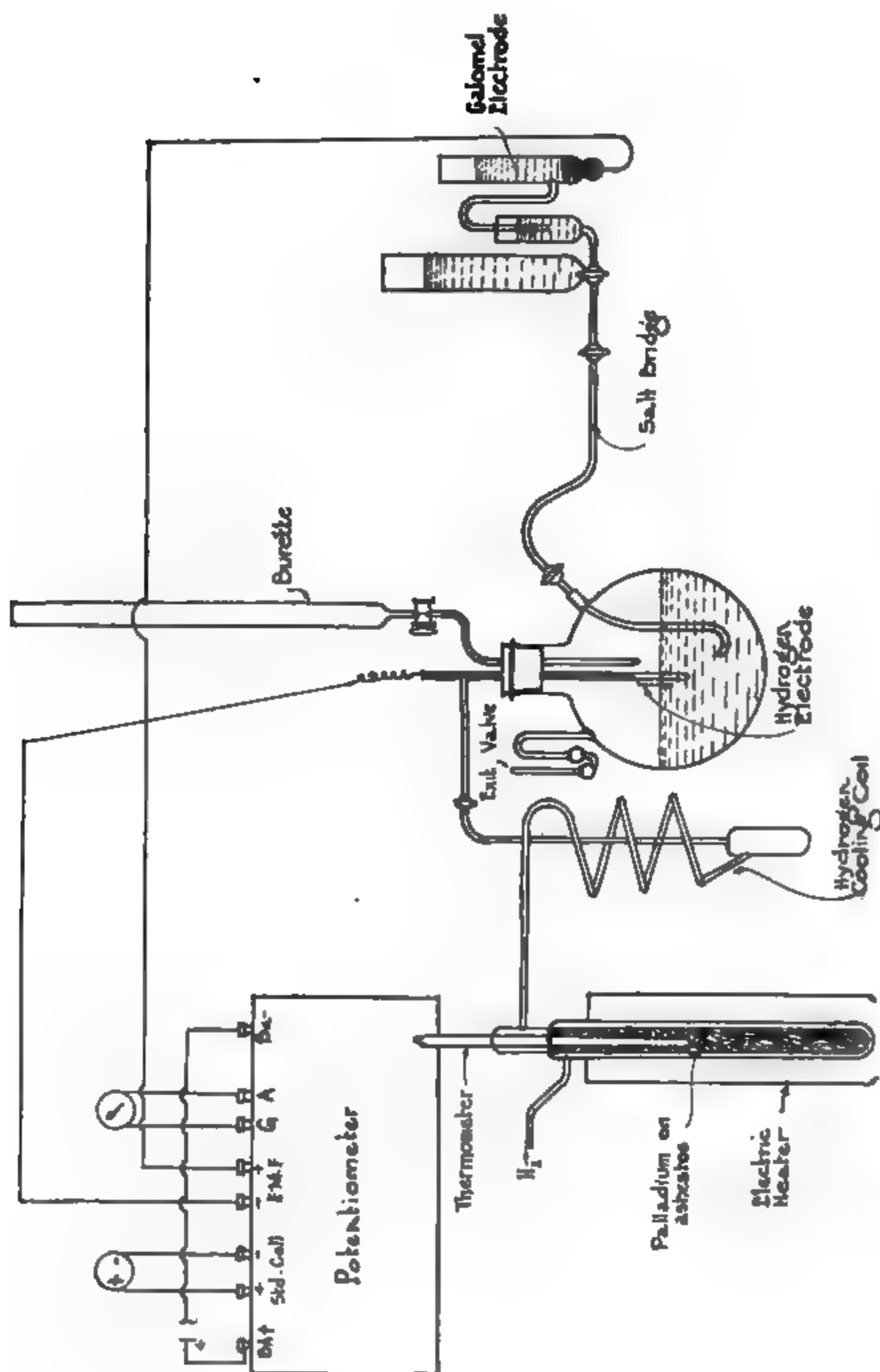


FIG. 224. Apparatus for electrometric titrations.

### The Electrometric Method of Titration in Oxidation and Reduction Reactions<sup>1</sup>

The electrometric method of oxidation and reduction titrations is similar to that for determining hydrogen ion concentrations since it is based upon the measurement of electrode potentials whereby relative ionic concentrations are determined.

In general, oxidation is a gain of valence or a loss of electrons while reduction is a loss of valence or a gain of electrons. The electric current may effect both oxidation and reduction, the former at the cathode where ions give up their electrons, and the latter at the anode where ions receive electrons, from the circuit. In a solution containing both ferrous and ferric ions the former will be oxidized at the cathode and the latter reduced at the anode. If no external electromotive force is applied and a single platinum wire is inserted into such a solution, the wire will acquire a positive or a negative potential, depending on the relative concentrations of the ferrous and ferric ions, the former tending to give up electrons, thus charging the wire negatively, and the latter tending to take electrons from it, thus giving the wire a positive charge. This can readily be demonstrated by connecting two such solutions possessing different relative concentrations of ferrous and ferric ions by a solution of potassium or sodium chloride and then connecting the electrodes in the solution by closing a circuit through a sensitive voltmeter. The voltmeter will now indicate a flow of current because the tendency for the ferrous ions to give up electrons will be relatively the greater in one solution, and the tendency for the ferric ions to take up electrons from the wire will be the greater in the other solution. The system therefore constitutes a cell whose potential can be measured. If the concentrations of ferrous and ferric ions could be kept constant in one of the solutions, it could become the standard whereby the ferric or ferrous ions of the other could be determined. Such a standard is experimentally impossible and instead of using such a system, a single ferrous-ferric solution is connected with a normal calomel electrode as follows:

Normal calomel electrode/saturated KCl sol./ferric-ferrous solution — Pt.

The potential of such a cell is given by the formula:

$$E = P + \frac{RT}{NF} \log_e \frac{C_o}{C_i}$$

$E$  = E.M.F. produced by the change from the "ous" to the "ic" state.

$P$  = a constant and is equal to the potential when the concentrations  $C_o$  and  $C_i$  are equal; thereby the second term of the second member becomes zero.

$C_o$  and  $C_i$  = the ionic concentrations of the lower and higher states of oxidation respectively.

$N$  = the increase or decrease of valence.

$R$  = gas constant = volts  $\times$  coulombs = 8316 joules.

$F$  = Faraday = 96,540.

$T$  = absolute temperature.

In the case of the ferrous-ferric cell the equation then becomes, after converting to common logarithms.

$$E = P + 0.058 \log \frac{C_o}{C_i}$$

<sup>1</sup> J. S. Coye.

By measuring the  $E$  of such a system when the ferrous and ferric ionic concentrations are equal and using a normal calomel electrode the value of  $P$  has been found to be .47 volts and the equation then becomes:

$$E = 0.47 + 0.058 \log \frac{C_o}{C_i}$$

The potential of such a system may thus be used as a measure of the relative concentrations of ferrous and ferric ions.

As an illustration, consider the case of titrating the ferrous iron in a hydrochloric acid solution with a standard solution of potassium bichromate, ferric iron being either absent or present. The potential at the beginning of the reaction will depend upon the nature and concentration of the anions as well as upon the concentrations of the ferrous and ferric ions. As the potassium bichromate solution is added the ferrous ions decrease and the ferric ions increase. The term  $0.058 \log C_o/C_i$ , which is the only varying term gradually decreases to zero when the concentration of ferrous and ferric ions become equal and then very slowly decreases until  $C_o$  becomes equal to zero when there is an abrupt change in voltage and the endpoint is reached. The endpoint may be readily redetermined by adding a slight excess of the potassium bichromate and titrating back with a standard solution of ferrous ammonium sulphate. A similar condition exists for all oxidation and reduction reactions. The constant  $P$  will, of course, be different for each reaction so that the potential readings will be different but the abrupt voltage change at the endpoint is common to all. Several forms of apparatus have been designed and described by different investigators for this type of work.

The advantages of this method are:

1. A high degree of accuracy can be obtained without sacrificing rapidity.
2. It is applicable to many reactions with only very slight adjustments.
3. The necessity of determining and making corrections for indicators is eliminated.
4. It is possible to determine very small amounts of iron and other metals possessing two states of oxidation, in many raw materials without employing the usual tedious methods of separation.

### The Kelley Electrometric Titration Apparatus<sup>1</sup>

The apparatus shown in Fig. 225 opposite this page was designed to indicate electrically the change of oxidation potential which occurs at the end-point in certain oxidation-reduction titrations. The principle is not new, but the apparatus combines in convenient form a number of parts which have been specially selected and tested for application to this use.

The apparatus consists essentially of a wooden case with an upright carrying the motor, burettes, stirrer and electrodes. In the case are two dry cells,

<sup>1</sup> G. L. Kelley, chemist, Midvale Steel and Ordnance Company.

"We are determining all chromium, vanadium and manganese in the Nicetown laboratory of this Company by this method, and with this apparatus. Our manganese and chromium determinations amount to about 2,000 to 2,500 each per month, and vanadium determinations probably number 500. The apparatus is also in use at the Carpenter Steel Company, where similar work is being carried out. I understand from Mr. Loos of that Company that it is giving excellent satisfaction there, and that it is their intention to put in additional apparatus. We, ourselves, use three pieces of apparatus for routine work and a fourth for research, which latter is practically continuous." Communicated to the editor.—G. L. KELLEY.

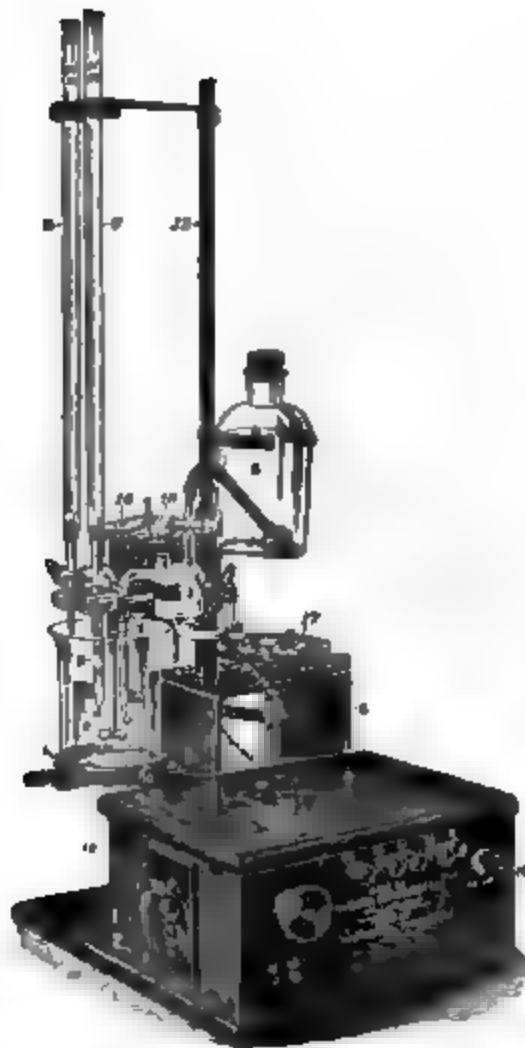


FIG. 225. Kelley's Electrometer.

an adjustable resistance and a reflecting galvanometer. On the upper surface of the case is a ground glass scale on which the light from the galvanometer is thrown. A knurled head shown at the side in Fig. 1 controls the adjustable resistance. Two switches are mounted on the sides of the case, one of which controls the galvanometer light and the motor driving the stirrer, while the other closes the potentiometer circuit. A rheostat (17, Fig. 1) is used to regulate the speed of the motor.

The operation of the apparatus depends upon the fact that when the platinum and calomel electrodes are placed in an oxidizing solution, such as chromic acid, a cell with certain definite electromotive force is produced. This electromotive force is balanced against a portion of the E.M.F. of two dry cells through a resistance and a slide wire. On adding even a slight excess of a reducing agent, such as ferrous sulfate, this balance is disturbed, the movement of the galvanometer indicating that the end-point has been reached. The change is a striking one, and may in some instances amount to .30 volt for .05 cc. of solution.

The apparatus as shown in the illustrations and as described above may be used for the determination of vanadium, chromium and manganese in steel by methods described elsewhere in this volume. It is also available for the determination of end-points in oxidation-reduction titrations where the reaction is rapid and the change in oxidation potential large. Bichowsky<sup>1</sup> has applied similar apparatus to the determination of zinc by precipitation with potassium ferrocyanide. This is an example of an application dependent upon precipitation by a strong reducing or oxidizing agent, in which the presence of an excess of the precipitant, even in small amount, produces a large change in oxidation potential. When the titration is a relatively slow one, such as the titration of ferrocyanide with permanganate, as described by Kelley and Bohn,<sup>2</sup> it is necessary to include some device for reading the change in potential near the end-point. A potentiometer bridge may be used or a voltmeter with a range of 1.5 volts arranged, as described by Hildebrand,<sup>3</sup> may be used to advantage. For the purposes mentioned above a calomel electrode (3) and a platinum electrode (9) are used as shown in Fig. 1.

In alkalimetric titrations a hydrogen electrode is substituted for the platinum electrode and the previously mentioned potentiometer bridge or voltmeter is used. Hildebrand<sup>4</sup> describes a number of such titrations.

In conductivity measurements a conductivity cell is used together with a Wheatstone bridge and an alternating current galvanometer. Harned and Laird,<sup>5</sup> Cain<sup>6</sup> and other investigators have outlined applications of conductivity measurements to analytical work. Provision is made for the convenient attachment to the apparatus of the necessary auxiliary parts when these are required.

<sup>1</sup> Jour. Ind. and Eng. Chem., p. 943, 9, 1917.

<sup>2</sup> Jour. Amer. Chem. Soc., p. 1776, 41, 1919.

<sup>3</sup> Jour. Amer. Chem. Soc., p. 869, 35, 1913.

<sup>4</sup> Loc. cit.

<sup>5</sup> Jour. Amer. Chem. Soc., p. 1213, 40, 1918.

<sup>6</sup> Jour. Ind. and Eng. Chem., p. 852, 11, 1919.

For the purpose of oxidation titration reactions the calomel electrode (3, Fig. 1) is best prepared by placing in the electrode about  $\frac{1}{4}$ " of clean mercury followed by a 1 or 2 g. of freshly precipitated calomel in suspension in N sodium sulfate solution. The reservoir is then filled with more of the same sulfate solution.

Best results are obtained after 24 hours standing. The platinum electrode should be cleaned in chromic and sulfuric acid solutions and dipped momentarily in ferrous sulfate solution. When it is in daily use it requires only occasional cleaning with chromic acid or hydrochloric acid.

To titrate, the beaker containing the unknown solution is placed on the pan (1, Fig. 2) which is then raised to the position shown in Fig. 1. Closing switches (12) and (16), Fig. 1, starts the stirring motor, lights the galvanometer lamp and closes the potentiometer circuit. The rheostat (17, Fig. 1) is adjusted until the rate of stirring is as rapid as possible without drawing air over the electrodes. By turning the knurled knob shown on the side of Fig. 1, the beam from the galvanometer is brought to position zero on the scale (18, Fig. 1). When dichromate solutions are used, the screw below the resistance control should be in the position marked zero, but in titrating permanganate solutions it should be in the position marked 50. The first setting gives a range of potential 0 to 1.0 volts, the second .75 to 1.50.

The reducing solution is now admitted from the burettes. The first additions may be made rapidly, decreasing the rate as the end-point is approached. The nature of the end-points varies with the substance titrated. In general, without the aid of some apparatus permitting of reading potential change, it is possible to determine end-points only when the reducing solution is added to an oxidizing solution in the beaker. The end-point in the chromate titration is generally an abrupt and permanent deflection, perhaps, preceded by a few momentary changes from which there is a prompt return. The titration of vanadium is characterized by a period of gradual change during the addition of the first half or three quarters of the ferrous sulfate solution. This change corresponds to a gradual slope in the potential curve. It is followed by a period in which the beam is almost at rest until the end-point is reached. Here there is a sudden permanent deflection, somewhat less marked than with chromate. The exact end-point is found by adding dichromate solution until the beam is returned to the former position, after which dropwise additions of ferrous sulfate produce a succession of small movements of the beam, the largest being taken as the end-point. When permanganate is titrated with mercurous nitrate, the beam maintains its position until the end-point is approached. It then moves rapidly off the scale with the addition of each drop, returning more and more slowly. When several seconds are required for its return, which may be after, perhaps, the fourth drop, the end-point is considered reached. The end-point obtained by titrating ferrous sulfate and potassium permanganate is described by Kelley, Adams and Wiley<sup>1</sup> and by Hostetter and Roberts,<sup>2</sup> the latter working with an apparatus of different design but similar principle.

<sup>1</sup> Jour. Ind. and Eng. Chem., p. 780, 9, 1917.

<sup>2</sup> Jour. Amer. Chem. Soc., p. 1337, 41, 1919.



### The Determination of Chromium in Steel by Electrometric Titration<sup>1</sup>

**Silver Nitrate Solution.** 2.5 g. silver nitrate in water to make one liter.

**Ammonium Persulfate Solution.** 100 g. ammonium persulfate in water to make one liter.

**Potassium Dichromate Solution.** 2.828 g. potassium dichromate in water to make exactly one liter.

**Ferrous Sulfate Solution.** 23 g. ferrous ammonium sulfate and 100 cc. of sulfuric acid (sp.gr. 1.58) in water to make one liter. Compare this solution daily with the dichromate solution. A factor may be used or the strength adjusted by adding water or salt.

**Solution of the Sample.** Take 2 g. samples of steel containing less than .50 per cent of chromium, 1 g. of those containing up to 5 per cent and  $\frac{1}{2}$  g. or  $\frac{1}{4}$  g. of those containing 5 to 25 per cent. Dissolve 1 g. or smaller samples in 70 cc. of hot sulfuric acid, sp.gr. 1.20, and 2 g. samples in 100 cc. The destruction of carbides, which are often present, is greatly assisted by rapid solution in boiling sulfuric acid. Other acids which might serve this purpose better are not otherwise suitable for the method. To insure the complete breaking up of carbides, all samples containing more than .5 per cent of chromium should be evaporated until salts separate. The solution may then be cautiously diluted with 50 cc. of hot water, when it is ready for oxidation by the addition of two or three cc. of nitric acid, added drop by drop to the boiling solution. The chromium carbides in tungsten steel are usually decomposed without evaporation until salts separate. Steels high in carbon and containing from 10 to 25 per cent of chromium may require after the oxidation with nitric acid a second evaporation until salts separate. The analyst should examine the solution for undecomposed carbides in all doubtful cases. Samples resisting the foregoing treatment may be successfully dealt with after solution in hydrochloric acid, and oxidation with nitric acid, followed by evaporation with sulfuric acid until fumes appear. All hydrochloric acid must be removed.

**Oxidation of Chromium.** When the decomposition of carbides is complete and the iron has been oxidized, the solution should be diluted with hot water to a volume of 250 to 300 cc. In this volume the concentration of sulfuric acid is high enough to prevent the precipitation of manganese as dioxide during the oxidation with ammonium persulfate, if the amount of manganese is not over one per cent. On the other hand, the concentration of sulfuric acid is not high enough to interfere with the oxidation of the chromium and manganese. Should the manganese exceed one per cent, a smaller sample may be used, or the solution may be diluted to a larger volume, making at the same time a sufficient addition of sulfuric acid to maintain the same concentration.

When the solution has been heated to boiling, add 10 cc. of the silver nitrate solution followed by 20 cc. of the ammonium persulfate solution. The success of the oxidation is indicated by the development of the color of permanganic acid, but there should not be more than a very slight turbidity from the formation of manganese dioxide. If this color does not develop and persist after two minutes boiling, more of the oxidizing solution should be added. The boiling is continued at least eight minutes. With high percentages of chromium in which the additions of persulfate are large a longer time increases the accuracy

<sup>1</sup> G. L. Kelley, chemist, Midvale Steel and Ordnance Company.

of the determination. In the presence of silver nitrate eight minutes boiling is usually sufficient to complete the breaking down of the smaller amounts of ammonium persulfate. After this and while the solution is still boiling, an addition of 5 cc. of one to three hydrochloric acid is made to decompose the permanganic acid. Should the hydrochloric acid be added too soon, the decomposition of any remaining ammonium persulfate gives rise to products which reduce the chromic acid. In this concentration, the hydrochloric acid can decompose no more than traces of manganese dioxide, for which reason the solution should be nearly clear at the time the addition is made. Five minutes is the minimum time of boiling for the decomposition of the permanganic acid, but a longer time is not harmful if the volume does not fall too low. After cooling, the solution is ready to titrate.

**Titration of the Solution.** Place the electrodes in the solution, and by adjusting the resistance, place the beam of light at that end of the scale toward which it tends to move as the oxidation potential of the solution under examination increases. Add the ferrous sulfate solution rapidly until the beam of light moves permanently in the opposite direction. Follow this with dichromate solution added dropwise until the beam will move no further in the direction of its original position. Ferrous sulfate solution is then added one drop at a time until the end-point is found. This is taken as the first drop at which there is a permanent movement of the beam away from the original position. During the latter operation the beam is usually stationary or nearly so until the end-point is reached. If the end-point is not sharp, this may be improved by adding 25 cc. of sulfuric acid.

Each cubic centimeter of the dichromate solution is equivalent to 0.10 per cent of chromium in a 1 g. sample. To calculate, convert the ferrous sulfate used into terms of dichromate, subtract the amount of dichromate actually added, and divide by the number of grams in the sample and by 10.

If vanadium is present, this also will be titrated. In such a case the end-point described under the vanadium titration should be used. To calculate the result, multiply the vanadium titration as found in the vanadium determination by .340 and subtract this from the titration of chromium and vanadium together.

#### References

- J. Ind. and Eng. Chem., p. 719, Vol. 8, 1916.  
Ibid., p. 780, Vol. 9, 1917.  
Ibid., p. 632, Vol. 11, 1919.

### Determination of Vanadium in Steel by Electrometric Titration<sup>1</sup>

**Dichromate Solution.** Dissolve .9609 g. potassium dichromate in water to make exactly one liter. 1 cc. corresponds to .10 per cent vanadium in a 1 g. sample. The factor for converting this dichromate solution into one in which 1 cc. is equivalent to .1 per cent of chromium in a one gram sample is .340.

**Ferrous Ammonium Sulfate.** Dissolve 8 g. ferrous ammonium sulfate and 100 cc. of sulfuric acid in water to make approximately one liter. Compare this solution daily with the standard dichromate solution.

**Procedure.** When the vanadium present is less than .5%, use a two gram sample, dissolving in 40 cc. sulfuric acid (sp.gr. 1.58) and 60 cc. water. When the vanadium is higher use a 1 g. sample, dissolving this in 30 cc. of sulfuric acid and 50 cc. of water. When solution is complete, oxidize with two to three cc. of nitric acid added gradually. Tungsten does not interfere if the given proportions of acid and water are adhered to, but under other conditions it may precipitate in such a way as to cause difficulty in titrating. Boiling after the addition of nitric acid should be continued until the tungsten appears to be well oxidized. The solution should then be diluted to 200 cc. volume and 40 cc. of conc. nitric acid added. It is then ready to be boiled at least one hour at such a rate that the final volume falls between 100 and 125 cc. Shorter boiling may give incomplete oxidation, but no danger attends longer boiling if the volume does not fall below 100 cc. Reducing the volume below this point may result in the oxidation of chromium. After cooling and diluting to 300 cc., the solution is ready for titration. The temperature should be 20° C. or lower.

During the titration, there is at first a gradual fall of potential. After a time the beam of light comes to rest. Continued addition of ferrous sulfate at length causes the beam to move again. When this occurs, enough chromate is added to cause its return. The dropwise addition of ferrous sulfate soon causes a succession of small movements followed by some larger ones, the largest of which is taken as the end point.

The directions given above result in the oxidation of 99 per cent of the vanadium in solution.<sup>2</sup> Accordingly this may be calculated by dividing by .99 or approximated by adding one per cent of the figure. When tungsten is present, a certain amount of vanadium is occluded by the tungsten oxide. This amounts to .015 per cent in steels containing 11 to 15 per cent tungsten and .02 per cent in those containing 20 per cent. This should be added to the amount found by titration.

#### Reference

Jour. of Indust. and Engrg. Chem., p. 19, 10, 1918.

<sup>1</sup> G. L. Kelley, chemist, Midvale Steel and Ordnance Company.

<sup>2</sup> See Jour. American Chemical Society, p. 341, 38, 1916, and Jour. of Indust. and Engrg. Chem., p. 632, 11, 1919.

### Determination of Manganese in Steel in the Presence or Absence of Chromium and Vanadium by Electrometric Titration<sup>1</sup>

**Solutions:** *Ammonium Persulfate.* Ammonium persulfate 100 g. and water to make one liter.

*Sodium Thiosulfate.* Saturated solution.

*Treated Three Per Cent Nitric Acid.* 30 cc. nitric acid, 1 g. sodium bismuthate and 970 cc. water.

*Treated Twenty-five Per Cent Nitric Acid.* 250 cc. nitric acid, 2 g. sodium bismuthate and 750 cc. water.

*Mercurous Nitrate.* Dissolve 10.5 g. mercurous nitrate in 2 cc. nitric acid and 150 cc. water. Decant the clear portion and make up to one liter. Adjust strength after five days to equal that of the permanganate solution.

*Potassium Permanganate.* 3 g. potassium permanganate in two liters of water. After a few days, filter through asbestos and adjust strength by the addition of water until 39.33 cc. is equivalent to .1200 g. Bureau of Standards sodium oxalate. It then contains .0005 g. Mn per cc. and 1 cc. is equivalent to .05 per cent Mn in a 1 g. sample.

**Procedure.** Dissolve 1 g. of steel in 50 cc. of nitric acid (sp.gr. 1.13), add 10 cc. of persulfate solution and boil until the persulfate is decomposed. Reduce the solution with thiosulfate and boil three minutes. Add 50 cc. of "treated 25 per cent nitric acid" and cool to 20° to 30° C. Oxidize with 1 g. of sodium bismuthate for at least one minute and filter through an asbestos mat on a perforated porcelain plate, washing the beaker and the mat with 100 cc. of "treated 3 per cent nitric acid." Oxidation should be continued long enough to insure the oxidation of all manganese. The oxidation of chromium is of advantage for it is not titrated by the mercurous nitrate under the conditions described, and as chromic acid it does not reduce the permanganic acid. Because of this, while there is no need for haste in filtering, it is important to titrate as soon as the bismuthate has been removed to avoid the reaction between the chromic salt and permanganate. The filtrate should be promptly added to a beaker containing cold water or ice and 50 cc. of sulfuric acid (sp.gr. 1.58) added. Titration is best made at a temperature of 20° C.

The permanganate and mercurous nitrate should be compared by titrating at least 20 cc. of the permanganate solution in a cool mixture made up of 50 cc. sulfuric acid, 150 cc. ice water and 100 cc. of "treated 25 per cent nitric acid." The solution must be free from sodium bismuthate. To titrate, place the beam of light on the scale. Near the end-point successive additions of mercurous nitrate cause the beam to leave the scale, after which it returns slowly. At length the beam remains off the scale at least 30 seconds. This may be taken as the end-point. If there is doubt, the addition of a few drops of permanganate causes its return. The end-point may then be found as before, or it may be taken as the addition which causes the beam to remain permanently at least five large divisions from the original position. Repeated back titration gives poor results.

To calculate, subtract the permanganate used, divide the result by 2, and move the decimal point one place toward the left.

<sup>1</sup> G. L. Kelley, chemist, Midvale Steel and Ordnance Company.

<sup>2</sup> Dissolve high chromium 15 per cent steels in hydrochloric acid and evaporate three times with nitric acid. Then proceed as usual.

<sup>3</sup> The presence of cobalt interferes with this titration. In such cases the manganese should be precipitated with ammonium persulfate by the known methods.

## BEAM TEST FOR DETERMINING THE PRESENCE OF SUSPENDED MATTER IN GASES<sup>1</sup>

Tyndall demonstrated that dust particles are responsible for the visibility of rays of light, such as the sun beam or the beam of the searchlight. He did not make clear the best conditions enabling one to see the beam produced by minute amounts of suspended matter in purified gases, nor did he show that a gas free of dust may still produce a beam in presence of liquid mist. The opinion commonly current regarding the conditions necessary to see the beam produced by light rays in purified gas, is that the rays should be parallel and should be viewed with the visual axis at right angles to this beam. Observing these conditions the author<sup>1</sup> failed to see the beam using direct sunlight, but discovered that a cone of light from an arc light gave a distinct beam. This led to the discovery that the beam is best viewed by glancing towards the source of light. Accordingly the apparatus shown in Fig. 226 was designed.

For the examination of a corrosive gas, it is advisable to have the chamber of the camera made of a material not affected by that gas. For example, in examining purified contact gas a lead chamber is recommended. The interior of the chamber is blackened with dull paint that is a poor light reflector. In the apparatus shown, circular glass discs close the ends of the tubes "a," "b" and "c." The gas examined enters near the eyepiece "b" and passes out at the opposite large end. The ray of light is directed through a small opening, either circular (diam. 1 cm.) or a narrow slit, located at "a" and passes through the arm of the tube and out through a glass window at "c." The idea is to avoid light reflection in the chamber, as this would cause a glow in the tube and greatly reduce the sensibility of the test.

The beam caused by liquid mist alone appears as a uniform pencil or band of light, whereas dust particles produce a sparkling effect or irregular flashes of light. The beam is more intense with the gas in motion. Within certain limits the intensity of the beam is directly proportional to amount of suspended matter in the gas.

If the gas is dry the beam is completely removed by passing the gas through a three-inch mat of loosely carded purified asbestos. If the gas, thus purified of solid matter, is passed through a liquid the beam again becomes apparent. From this it is evident that the test must be applied to dry gas if it is desired to ascertain the presence of solid matter in suspension.

Fig. 230 shows the apparatus set up for ascertaining the effectiveness of a scrubber in a quantitative determination of the solid and liquid suspended matter in a gas. The apparatus is so arranged that comparisons may be made of the unfiltered gas, by means of a bypass with that of the filtered or purified gas. Advantage is taken of the difference in pressures at A and B, so that a continuous sample may be taken of the gas without the necessity of an aspirator. A hand arc light shown on the left furnishes the rays of light which enter at "a" and pass out into the air at "c." The beam is viewed through the eyepiece "b." The meter measures the volume of gas aspirated.

<sup>1</sup> Contributed by Wilfred W. Scott.

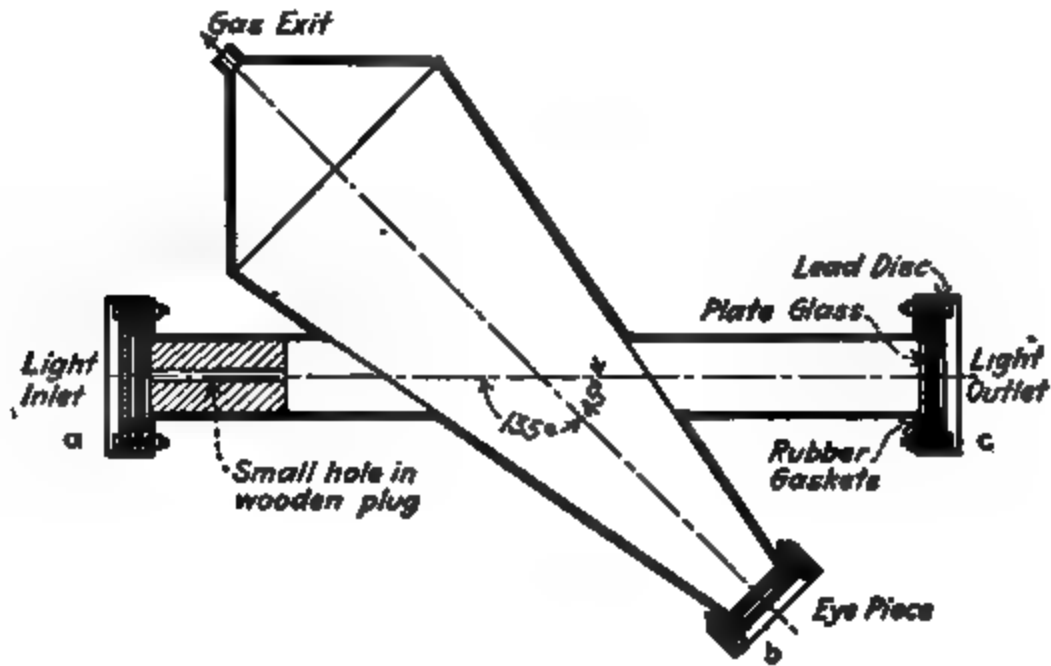
**Beam Test for Suspended Matters in Gases.**

FIG. 226.

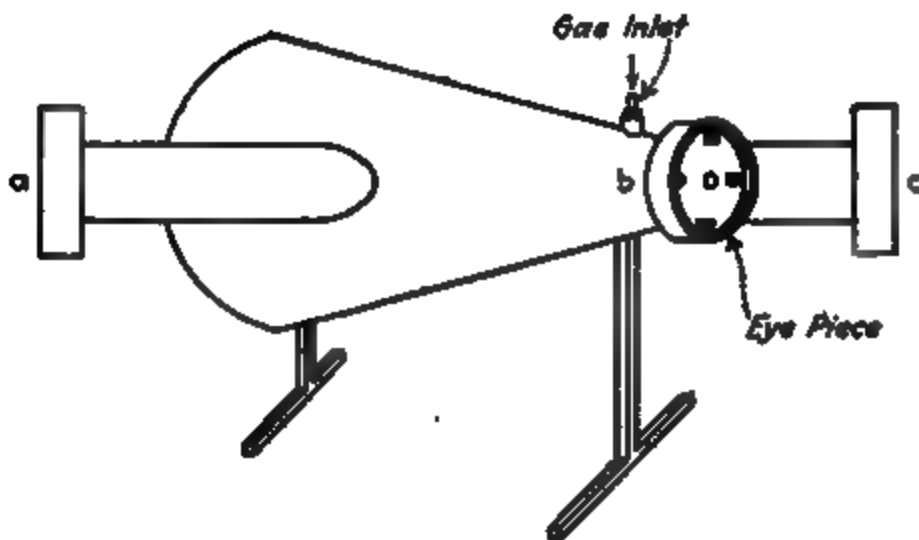


FIG. 227. Apparatus for ascertaining the pressure of suspended material in a gas by means of a beam of light.

## DETERMINATION OF SOLID AND LIQUID IMPURITIES IN A GAS<sup>1</sup>

Solid or liquid impurities suspended in a gas may be removed quantitatively by passing the gas through a filter of loosely carded dry asbestos. A filter two inches thick and  $1\frac{1}{4}$  inches in diameter is effective in removing suspended matter completely with gas passing through it at the rate of 2 to 3 liters per second (5 to 7 cubic feet per minute). It is essential that the asbestos be free from condensed moisture as a soggy filter is not effective for gas filtration.

**Determination of Sulphuric Acid Mist in Gas.** The gas is aspirated through a filter of well-carded, blue fibre, purified asbestos, the asbestos extracted with water and the extract titrated with standard alkali.

**Apparatus.** An ordinary  $1\frac{1}{4}$  inch filter tube funnel (see Fig. 229) with long stem, to permit a sample being drawn directly from the flue may be used. If the gas is supersaturated with moisture it is advisable to use the form of apparatus shown in Fig. 228, the bottle serving as a condensing chamber to avoid water condensation on the asbestos. Occasionally it is necessary to pass the gas through two such chambers to remove the condensed moisture from warm moist gases.

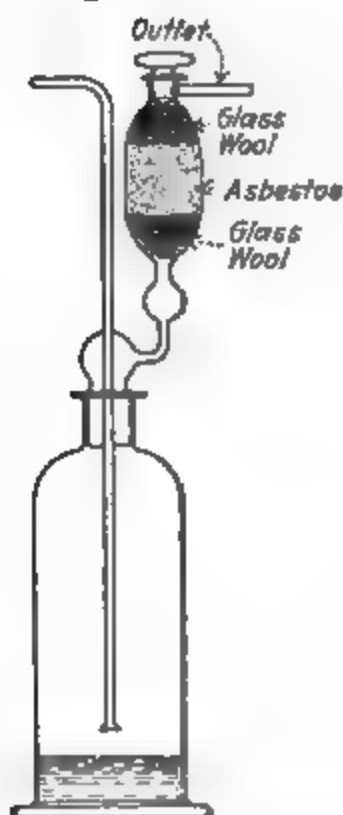


FIG. 228. Apparatus for determining solids and liquid mist in wet gases.

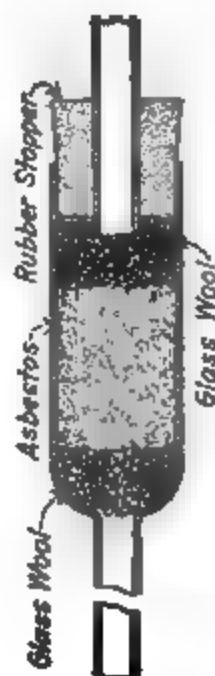


FIG. 229. Filter for gases.

The funnel is packed first with a layer of glass wool, followed by a two-inch layer of well-carded, purified, blue asbestos, and finally a second layer of glass wool. The glass wool prevents the asbestos plugging the inlet and exit openings. Perforated disks may be used in place of the glass wool.

The asbestos is the blue African form. White asbestos will not give accurate results as this is attacked slightly by dilute sulphuric acid and decidedly so by strong sulphuric. The blue form is not appreciably attacked so that the acid may be extracted as free acid by water. The asbestos is purified by digesting with nitric acid, followed by a second digestion with hydrochloric

<sup>1</sup> Contributed by Wilfred W. Scott.

## Impurities in Gases.

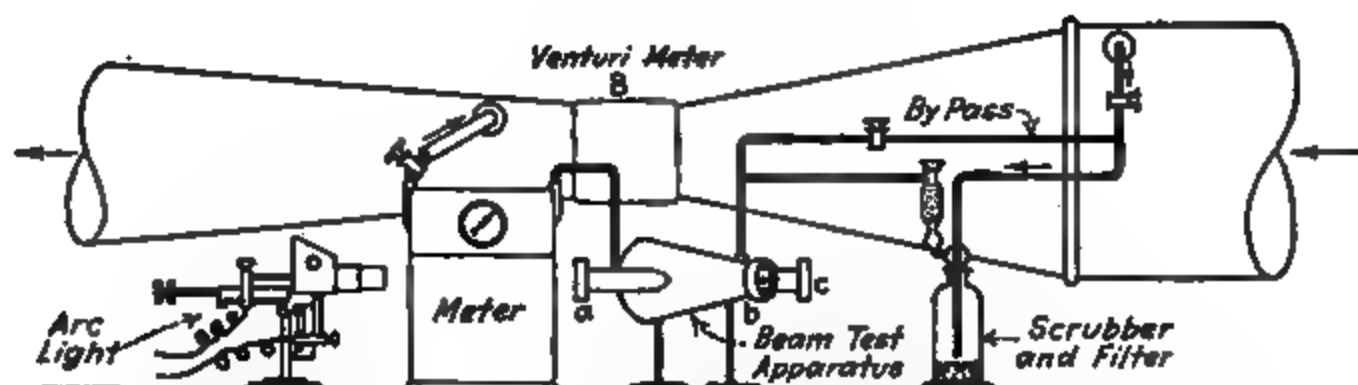


FIG. 230. Apparatus for determining solid or liquid impurities in gases.

acid. The material is now thoroughly washed to remove the acids and is dried. The dry asbestos is placed in wide mouth bottles until required. Before using it is carded or fluffed out by means of a pick and then placed loosely in the funnel to be used in the test.

**The Test.** The gas is aspirated through the filter at the rate of about five cubic feet per minute, the gas being measured by a dry gas meter following the apparatus. When a volume of 10 to 100 cubic feet of gas has been aspirated, the amount depending upon the amount of acid mist present in the gas, the asbestos filter is placed in a beaker. (If  $\text{SO}_2$  is present in the gas, as is the case in contact sulphur gases, air is first passed through the asbestos to remove the  $\text{SO}_2$ .) The tube is rinsed out, the rinsings added to the asbestos. The contents of the beaker is now transferred to a two-inch Buechner funnel in position on a half-liter capacity suction bottle. The water is drawn out of the asbestos and the filtrate passed through the mat, thus formed, to remove the asbestos fibers. The mat is washed with small portions of pure water, until free of acid and the extract, transferred to a beaker, is titrated with standard alkali. N/20 alkali has been found to be satisfactory. Methyl orange is used as an indicator.

**Determination of Arsenic in Gas.** The test is the same as the one described for determining sulphuric acid. An aliquot portion of the water extract is taken for a Gutzeit determination of arsenic. The Gutzeit method is described in full in the chapter on arsenic, Volume I. Arsenic in purified contact gas is carried in the acid mist.

**Determination of Chlorides.** A portion of the water extract, obtained by the procedure described under the test for acid in gas and filtered through paper if necessary, is examined for chloride by the turbidity test by addition of nitric acid followed by silver nitrate reagent. Comparison is made with a standard using either Nessler tubes or a colorimeter. If the amount of chloride is too great for a turbidity test a gravimetric determination should be made, or the aliquot portion taken should be sufficiently diluted with water to enable the turbidity test to be made. The standard should contain the same amount of sulphuric acid as the sample. The extract should be free of asbestos fibre.

## Composition of Asbestos.

* Asbestos	$\text{SiO}_2$	$\text{CaO}$	$\text{MgO}$	$\text{FeO}$	$\text{Al}_2\text{O}_3$	$\text{MnO}$	$\text{H}_2\text{O}$
Blue—African	49.0	1.2	2.7	24.4	11.9	—	—
White—Canadian	40.3	—	43.4	.9	2.3	—	13.7
White—Italian	55.9	17.8	20.3	—	4.3	1.1	—



# RADIUM

L. D. ROBERTS<sup>1</sup>

## Detection

Radium discharges the electroscope of the alpha ray instrument. However, other radioactive elements do also. There are only three elements that give a gas called emanation as a product. These elements are actinium, radium and thorium. They can all be distinguished by collecting the gas and observing its rate of decay. The time required for one half of the gas to decay is known as the half-period. The half-period of actinium emanation is 3.9 sec., radium emanation 3.85 days, thorium emanation 54 sec. In preparing samples for the alpha ray test they should be ground to about the same mesh. If the sample causes the leaf to move faster than it moves when the chamber is empty, the specimen is radioactive. The time is taken with a stop-watch.

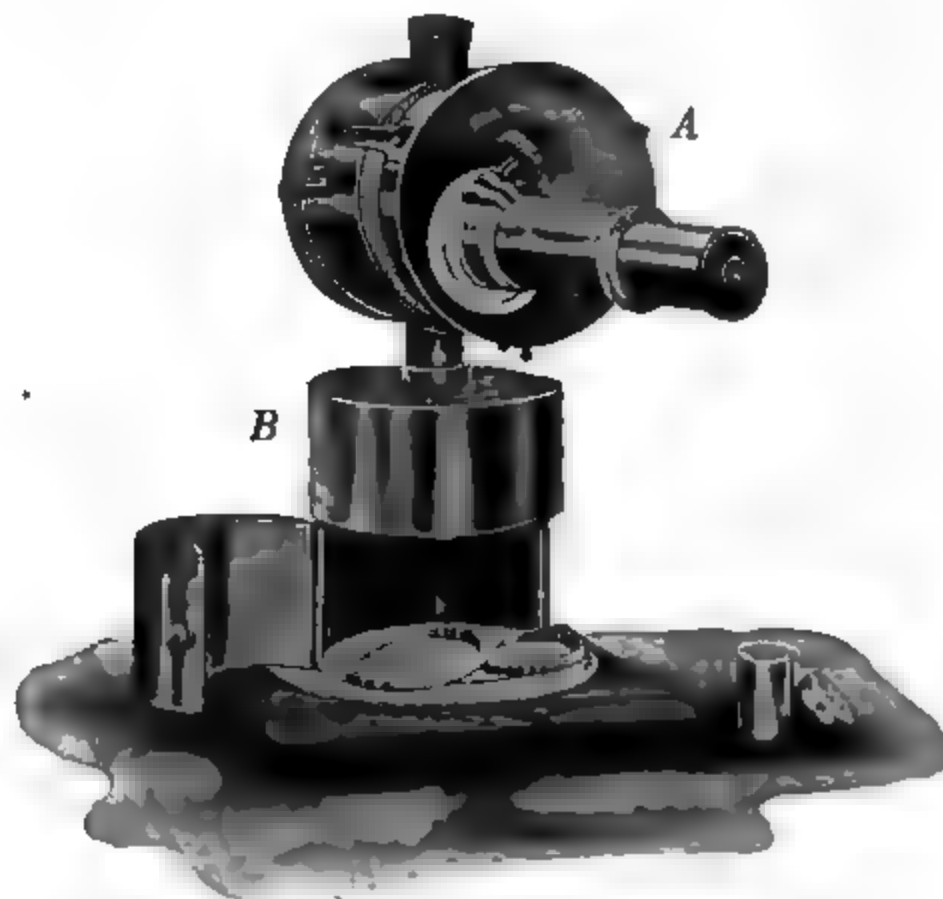


FIG. 231.

## Estimation

Radium is determined by the following methods: I, Alpha Ray; II, Emanation; III, Gamma Ray. The determination with the alpha ray instrument is only approximate and depends on having the samples in the same physical condition as much as possible. The discharge of the leaf is influenced by the fineness of the sample. Also the compound that the element is found in makes a difference. The emanating power of radium chloride is greater than that of radium sulfate, or oxalate. This method is used in the mining camps because it is simple and requires very little equipment. The emanation method is more accurate and is usually used at the plant and laboratory. The

<sup>1</sup> Associate Professor of Chemistry, Colorado School of Mines

gamma ray method is used when the sample cannot be removed from its container, and also for very high grade material. Tubes of emanation prepared for therapeutic use are determined in this way.

### The Alpha Ray Method

The alpha ray instrument consists of an electroscope head *A* (Fig. 231) and the chamber *B*. Head *A* contains an aluminum or gold leaf attached to a metal rod and a reading telescope so placed as to read the deflection of the leaf when charged. *B* is the chamber to receive the sample. A spring from the metal rod in *A* connects this with a rod which extends into *B*. On the end of the latter is placed a disk. The rays discharge the leaf through this disk and rod. The rod in the chamber is insulated from the case with amberoid, made by subjecting amber powder to great pressure. *A* is charged by means of a battery, or an ebonite rod can be used. The battery is made by connecting seventy-five to a hundred French cells (or Eveready Tungsten No. 703) of about five volts each in series. It is best to ground the negative end and connect *A* by a floating wire to the positive pole of the cell which will give the desired deflection of the leaf. The case of the chamber is connected to the ground wire. A tube of distilled water is placed in the circuit to prevent the shorting of the batteries. Care should be taken not to charge the leaf enough to throw it against the case. The "natural Leak" is found by taking the time for the leaf to move over forty divisions, and calculating the divisions per second. Less than forty divisions may be taken if the time for forty divisions is quite long. If the leaf moves at the same rate over the whole scale, any part may be taken. The sample is placed in the plate for solids, and this is made exactly level full. The plate containing the sample is placed in a pan to protect the instrument from receiving active matter. The pan with its contents is now placed in the chamber *B*. As the charged leaf passes 8 (or some other chosen starting place) the stop watch is started. The watch is stopped at 4. The rate of discharge is calculated in divisions per second, and the natural leak is subtracted. A standard is run in exactly the same way. Since the rate of discharge is directly proportional to the amount of radium present, the amount of radium in the sample may be found by comparing its rate of discharge with that of the standard. This method gives approximate results. If the samples are of the same general character, the results may be in very good agreement, checking those obtained by the emanation method very closely.

### Emanation Method

**I. Carbonate Fusion.** About 2 grams of a mixture of sodium and potassium carbonates are placed in a platinum boat about 2 in. long,  $\frac{1}{2}$  in. wide and



FIG. 232.

$\frac{1}{2}$  in. deep. Larger boats may be used for low grade samples where large amounts are taken for analysis. From 0.05 to 1 gram of the sample should be weighed in the boat. The boat is now filled level full of the fusion mixture. The fusion is made over flame, or better, in an electric furnace at about 1000° C.

The boat should be put in the furnace while the furnace is cool. This will allow the fusion to dry and melt slowly, thus tending to prevent "boiling" over. The analyst will learn by practice how fast to heat up the furnace. When thoroughly fused and while still at the highest temperature, suddenly chill the fusion by dipping the boat in water, being careful not to allow water to run into the boat and wet the fusion. This chilling causes the mass to draw away from the boat and in the acid treatment slip out of the boat. The mass

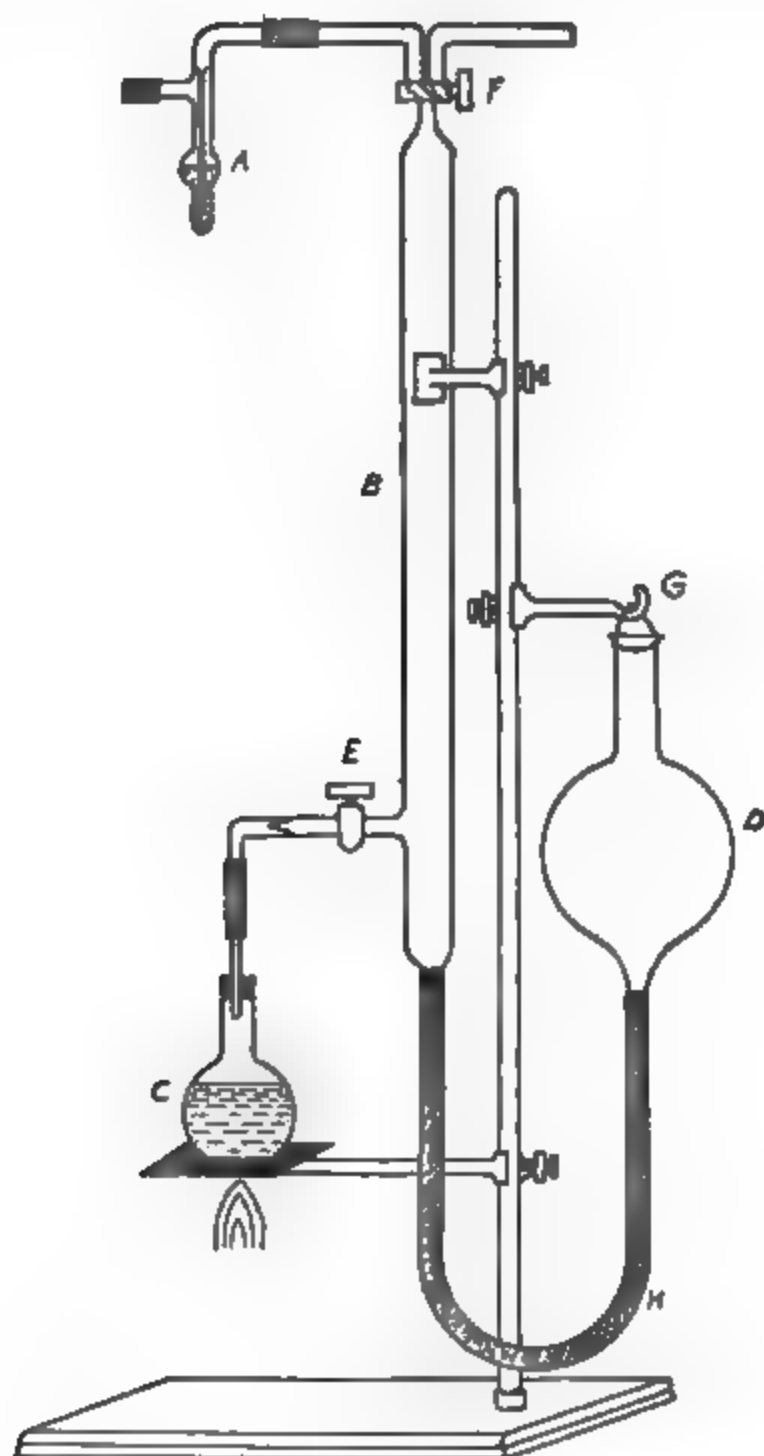


FIG. 233.

is also made more porous so that the acid attacks it much better. If very little silica is present, the chilling is not necessary. However, it does no harm. The boat with the fusion is sealed in a glass tube as shown in Fig. 232. The tube should be no larger than necessary. A number of tubes should be prepared in advance by having one end sealed. After standing from one to five or more

days (this time depends on the amount of radium present and on the time the result is demanded, the fourth day is usually about right; this gives a little more than a 50 per cent. recovery of the emanation), the emanation surrounding the boat is drawn into an evacuated chamber. The chamber may be evacuated by means of an aspirator on the water faucet or by a pump. To draw the emanation from the tube to the evacuated chamber a rubber tube



FIG. 234.

is placed on one end of the sealed tube and connected to the chamber with a capillary tube intervening to prevent broken glass from being drawn into the chamber, and a glass stopcock is connected by a rubber tube on the other end. The tip of the sealed tube next to the chamber is broken with a pair of pliers and the stopcock of the chamber opened for an instant. The other tip is broken and the glass stopcock opened for an instant. The stopcock of the chamber is opened again and closed after an instant. Air is let in through the glass stopcock again. After air is taken through about three times the chamber is ready to receive the emanation from the burette. It is necessary to use only a small part of the vacuum to draw the emanation from the sealed tube. The tube is broken and the boat is folded in a filter paper in such a manner that the paper will hold the boat in the neck of the flask until the flask is connected

with the apparatus as shown in Fig. 233. About 4 in. of a stick of sodium hydroxide is placed in the leveling bulb *D*. Boiling water is poured on this and the solution is raised in the burette about three-fourths of its height, having stopcock *E* closed and *F* open. *F* is now closed and the leveling bulb hung on hook *G*. Flask *C* contains 1-1  $\text{HNO}_3$ ; or if the fusion is hard to disintegrate 3 parts of acid to 2 of water is used. The boat is shaken into the nitric acid and stopcock *E* opened immediately. A bunsen burner flame is applied to the flask and the acid brought to boiling. The boiling is continued for 10 to 30 minutes according to the nature of the fusion. The heating must be regulated so that the solution in the burette is not driven too low. If the flask is heated too strongly the gas may be prevented from escaping through tube *H* by raising leveling bulb *D*. The burette is now connected to the chamber by means of a micro-drying bulb *A* containing sulfuric acid. The stopcock of the chamber is opened very slightly. Then the stopcock of the burette is opened slowly but fully. The stopcock of the chamber is now regulated till the flow of gas is such that the liquid in the burette rises steadily but not too fast. When the liquid rises to the stopcock the stopcock is turned and air let in till the level is about one-fourth down the tube. The air is drawn into the chamber till the liquid again reaches the stopcock. The air is again let in as before. The stopcock is opened into the chamber again and the liquid poured out of the leveling bulb. Air is drawn through the column till the chamber is full. The burette is disconnected, and the chamber set away to be read at the end of three hours. Just before time to make the reading the electroscope head is placed on the chamber and charged for fifteen minutes, and the chamber is opened to atmospheric pressure by opening the stopcock for only an instant, Fig. 234. From three to ten readings with the stop watch are taken over forty small divisions, say from 8 to 4. The temperature and pressure are noted. If these vary greatly from the conditions at which the instrument was standardized, the correction of the discharge must be made. The rate of discharge will be proportional to the pressure and inversely proportional to the temperature. The discharge is calculated in divisions per second. The natural leak, or still better, the blank is subtracted from this. This discharge is compared with that of a standard.

#### Example of a Determination and Calculation.

0.5 g. of sample sealed Oct. 1 at 5:00 P.M.		
Boiled off	Oct. 5 at 8:30 A.M.	
Time of recovery 3 days, 15½ hours		
Recovery factor for 3 days, 15 hr.	0.47926	See table.
	½ hr.	0.00193
	<hr/>	
	0.4812	
log. of	0.4812	-1.6822
colog. of	0.4812	.3178

A-II Time of discharge over 40 divisions of head A on chamber II. 92.5 sec

B-II Time of discharge over 40 divisions of head B on chamber II. 100 sec.

1.6021 log. of 40

1.9661 log. of 92.5

---

-1.6360	-1.6330 log of 0.4295
.4325	-9.9450 standardization of instrument
.0030 blank	.3178

---

	.3010 to change $\frac{1}{2}$ g. to gram.
.4295	2.6567 to change grams to pounds
	3.3010 to change pounds to tons

---

-2.1545

14.3 mg. of radium per ton.

B-II is calculated in the same way. The standardization of this particular instrument was -9.9825. The last four numbers are the same in the two cases. The number for the standardization of the instrument is the log of the number of grams of radium necessary to discharge the leaf one division per

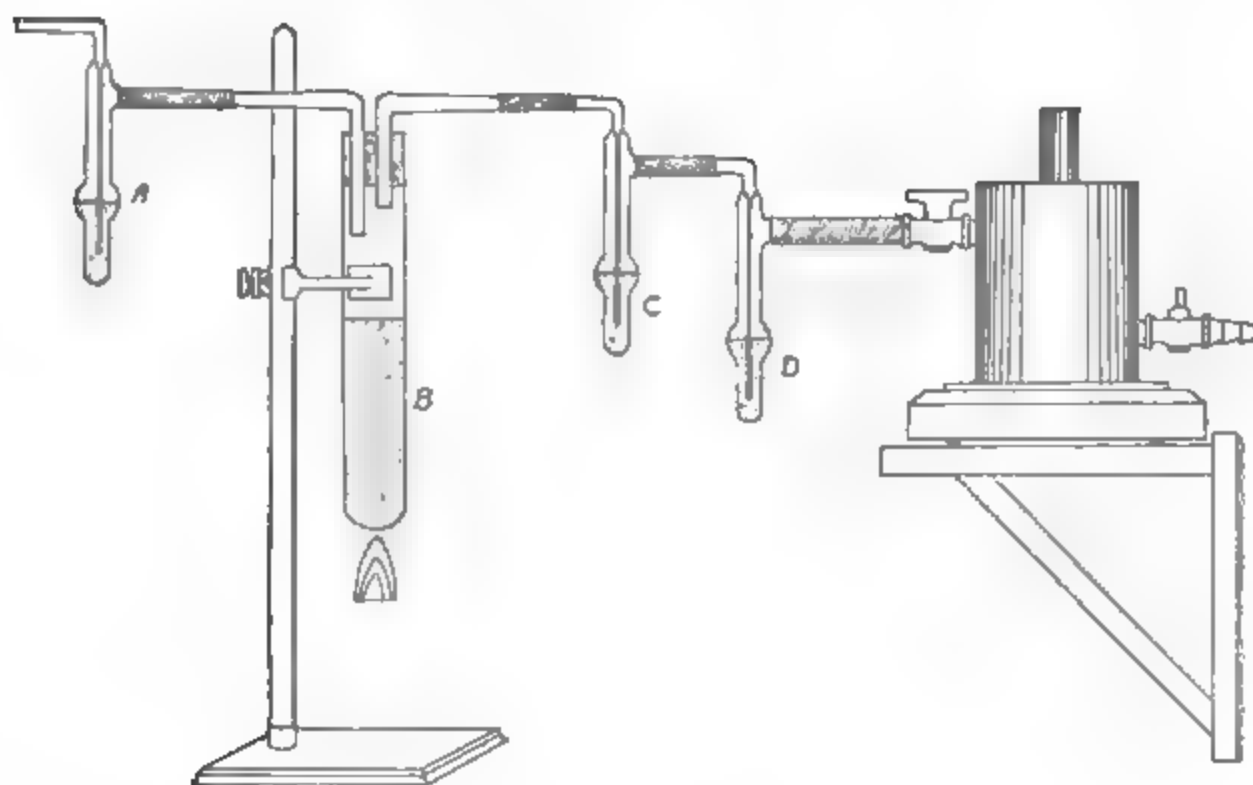


FIG. 235.

second. This is obtained by running through the instrument pitchblende or a radium solution the radium content of which is accurately known. In all cases the natural leak or a blank must be subtracted.

The instrument is charged 15 minutes before the readings are made in order to allow the active deposits of Radium A, B and C to collect on the wall of the chamber. The leaf system should be charged positively. The readings are taken at the end of three hours after the emanation is drawn into the chamber because the activity increases to a maximum at that time. For the first part of the period the increase is very rapid. The maximum is actually reached at the end of four hours, but between three and five hours the change is very slow.

As soon as the readings are made the instruments must be freed from emanation by drawing dry air through them, the air being dried by sulfuric acid.

**II. Bisulfate Fusion.** A pyrex test tube 1.1/8 in. in diameter and 8 in. long is filled about  $\frac{1}{4}$  full of fused potassium bisulfate. Sodium bisulfate or a mixture of both potassium and sodium bisulfates may be used. From 0.05 to 5 grams of the finely ground sample should be added, the amount depending on the radium content of the sample. The tube is filled about  $\frac{3}{4}$  full of potassium bisulfate. In adding the last bisulfate care should be taken to carry down any of the sample adhering on the side of the tube. The mixture is now thoroughly fused, continuing till reaction is complete. The test tube is removed from the flame and held in a nearly horizontal position and slowly turned while the melt solidifies. A very small amount of barium carbonate is dropped into the tube. About  $\frac{1}{4}$  of a gram is sufficient. In cases of carnotite ores, slimes, and tails the fusion will be yellow. As soon as the tube is cool enough to be handled a rubber stopper carrying two outlet tubes drawn out to rather fine tips (see figure) is inserted. If this is done as soon as possible there will be a partial vacuum in the tube when it cools and this will indicate when the emanation is taken off that there has been no leak. One of the outlet tubes should extend about one fourth way down the test tube and the other just through the stopper. After emanation has recovered at least one day the tube is connected to an evacuated chamber as shown in Fig. 235. Micro-drying bulb *A* contains water or sulfuric acid and acts as an indicator to show when the current of air into the chamber is correctly regulated. *B* contains the fusion; *C* sodium hydroxide solution; *D* sulfuric acid. The tip near *A* is broken with a pair of pliers. On account of the vacuum in *B* air rushes through *A*. Immediately after breaking the first tip the second should be broken. The stopcock of the chamber is slowly opened till air bubbles rather slowly through *A*. The tube containing the fusion is carefully heated until all the fusion is melted. It is boiled for at least five minutes, or till the chamber is about to atmospheric pressure. During the heating, a steady current is maintained throughout the heating by regulating the stopcock of the chamber. The chamber is disconnected and set away to be read at the end of three hours. The procedure is the same from this point as in the carbonate fusion method.

### The Gamma Ray Method

The sample is placed in the holder at such a distance as will cause a reasonable rate of discharge—about one division per second. A standard is then placed at the same distance and the two rates of discharge compared. The natural leak should be subtracted from each reading. The quantities of radium are proportional to the rates of discharge.

In the gamma ray instrument the lead plate and the brass case of the chamber stop all the radiation except the gamma rays.

See Fig. 236.

### Method for Solutions

A measured volume of the solution is placed in a 150 cc. pyrex flask and dilute nitric acid added, filling the flask about one-half full. A little barium nitrate should be added to prevent the precipitation of radium sulfate. The solution is boiled to expel all the emanation. In the Colorado School of Mines

a special flask with a long  $\frac{1}{4}$  in. neck is used. This is sealed off in the flame while the solution is nearly boiling. The ordinary flask may be used by inserting a rubber stopper carrying a tube which can be sealed. Or the neck of a pyrex flask can be drawn out and sealed. With the rubber stopper the emanation sometimes leaks. The special flasks are made by the Denver Fire Clay Company. After the emanation has recovered for one or more days the flask is connected to the burette by a light-walled rubber tube as in Fig. 233. The tip is broken and heat is applied to the flask. On breaking the tip the rubber

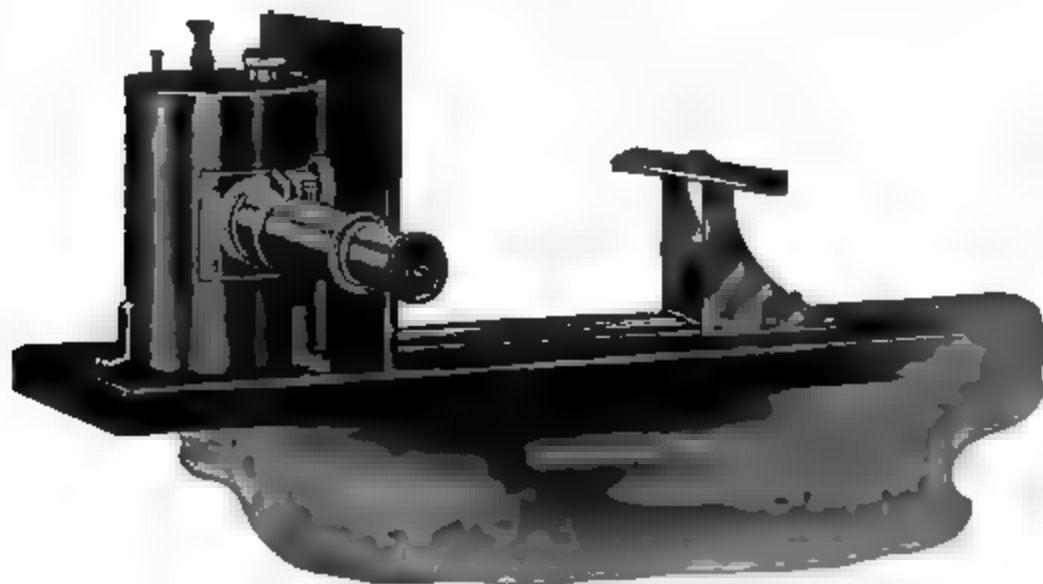


FIG. 233.

tube collapses if the flask has not leaked. When the pressure in the tube is about atmospheric the stopcock is opened slightly from time to time until the gas goes into the burette, and then opened wide. The solution is boiled for about ten minutes. The gas is then drawn into an evacuated chamber, as described in the other methods. The calculation may be made in milligrams per liter.

#### Notes

The carbonate method is similar to that given in bulletin 104, U. S. Bureau of Mines.

The bisulfate method of which the method here given is a modification was first published by Howard H. Barker in the Journal of Industrial and Engineering Chemistry for July, 1918, and improved by the Radium Company of Colorado.

Radium is found principally in carnotite and pitchblende. The largest carnotite deposits in the world are in southwestern Colorado and southeastern Utah. Uranium ores contain radium; the ratio of radium to that of uranium is  $3.4 \times 10^{-7}$ ; or, there are 3.4 parts of radium to 10,000,000 of uranium.

Radium salts correspond chemically to those of barium. In water barium sulfate is 100 times as soluble as radium sulfate.

Radium is used in the treatment of certain malignant growths and in luminous paints. Some of the radioactive elements have furnished the means of studying atomic structure.

Emanation should not be allowed to remain in the chambers any longer than is necessary. Air dried by sulfuric acid should be drawn through them.



The percent of  $U_3O_8$  multiplied by 2.6 gives the milligrams of radium per ton in ores. This holds good unless the ratio has been disturbed by leaching or some other cause.

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TABLE OF RADIUM EMANATION RECOVERY (KOLOWRAT)

t		Quantity Formed $1 - e^{-\lambda t}$	$\Delta$ per hour 0.00	t		Quantity Formed $1 - e^{-\lambda t}$	$\Delta$ per hour 0.00	t		Quantity Formed $1 - e^{-\lambda t}$	$\Delta$ per hour 0.00
Days	Hours			Days	Hours			Days	Hours		
	0	0.00000	747	2	4	0.32294	504	9	8	0.81363	1377
	1	0.00747	742	2	6	0.33302	498	9	12	0.81913	1326
	2	0.01489	736	2	8	0.34295	489	9	18	0.82709	1268
	3	0.02225	730	2	10	0.35274	482	10	0	0.83470	1212
	4	0.02955	725	2	12	0.36237	475	10	6	0.84197	1159
	5	0.03681	719	2	14	0.37187	468	10	12	0.84893	1108
	6	0.04400	715	2	16	0.38122	461	10	18	0.85558	1059
	7	0.05115	709	2	18	0.39041	454	11	0	0.86193	1013
	8	0.05824	703	2	20	0.39950	447	11	6	0.86801	9908
	9	0.06527	699	2	22	0.40844	440	11	12	0.87381	0925
	10	0.07226	693	2	24	0.41725	432	11	18	0.87937	0845
	11	0.07919	688	3	0	0.43022	422	12	0	0.88467	0840
	12	0.08607	683	3	6	0.44280	413	12	6	0.88975	0809
	13	0.09290	678	3	12	0.45529	404	12	12	0.89460	0775
	14	0.09968	672	3	18	0.46741	395	12	18	0.89924	0739
	15	0.10640	668	3	24	0.47926	386	13	0	0.90367	0701
	16	0.11308	663	3	30	0.49084	378	13	6	0.90928	0660
	17	0.11971	657	3	36	0.50217	369	13	12	0.91457	0622
	18	0.12628	653	4	0	0.51325	361	14	0	0.91954	0586
	19	0.13281	648	4	6	0.52408	353	14	6	0.92423	0552
	20	0.13929	643	4	12	0.53467	345	14	12	0.92864	0519
	21	0.14572	639	4	18	0.54502	337	15	0	0.93279	0489
	22	0.15211	633	4	24	0.55514	330	15	6	0.93671	0461
	23	0.15844	629	4	30	0.56504	323	15	12	0.94039	0434
1	0	0.16473	624	4	36	0.57472	315	16	0	0.94387	0409
1	1	0.17097	620	4	42	0.58418	308	16	6	0.94713	0385
1	2	0.17717	614	5	0	0.59343	3004	16	12	0.95021	0362
1	3	0.18331	611	5	6	0.60545	2915	17	0	0.95311	0341
1	4	0.18942	605	5	12	0.61711	2829	17	6	0.95584	0321
1	5	0.19547	601	5	18	0.62842	2745	17	12	0.95841	0300
1	6	0.20148	597	5	24	0.63941	2664	18	0	0.96084	0261
1	7	0.20745	592	5	30	0.65006	2585	18	6	0.96421	0257
1	8	0.21337	588	6	0	0.66040	2509	18	12	0.96729	0235
1	9	0.21925	583	6	6	0.67044	2435	19	0	0.97010	0214
1	10	0.22508	579	6	12	0.68018	2363	20	0	0.97268	0196
1	11	0.23087	575	6	18	0.68963	2293	20	6	0.97503	0179
1	12	0.23662	570	6	24	0.69881	2225	21	0	0.97718	0164
1	13	0.24232	567	6	30	0.70771	2160	21	6	0.97914	0150
1	14	0.24799	562	7	0	0.71635	2096	22	0	0.98094	0137
1	15	0.25361	557	7	6	0.72473	2034	22	6	0.98258	0125
1	16	0.25918	554	7	12	0.73286	1974	23	0	0.98408	0114
1	17	0.26472	549	7	18	0.74076	1915	23	6	0.98545	0104
1	18	0.27021	545	7	24	0.74842	1859	24	0	0.98670	0095
1	19	0.27566	542	7	30	0.75586	1804	24	6	0.98784	0087
1	20	0.28108	537	8	0	0.76307	1751	25	0	0.98885	0080
1	21	0.28645	533	8	6	0.77007	1699	25	6	0.98985	0073
1	22	0.29178	529	8	12	0.77687	1649	26	0	0.99072	0064
1	23	0.29707	525	8	18	0.78341	1600	27	0	0.99225	0053
2	0	0.30232	522	8	24	0.78961	1553	28	0	0.99353	0044
2	1	0.30754	517	8	30	0.79607	1507	29	0	0.99459	0037
2	2	0.31271	514	9	0	0.80210	1462	30	0	0.99548	
2	3	0.31785	509	9	6	0.80795	1419			1.00000	

Figures 232, 233 and 235 were drawn by M. Ettington.

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